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Studies on the Mannich Reaction. I. On the Formation of Piperidine Derivatives (1)

By Norito UCHINO

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(Received January 30, 1959)

The Mannich reaction of acetophenone with ammonium chloride and formaldehyde[1-3] gives hydrochlorides of mono-(β-benzoylethyl)-amine (I), bis-(β-benzoylethyl)-amine (II), tris-(β-benzoylethyl)-amine (III) and a small quantity of 4-hydroxy-4-phenyl-5-benzoyl-1-(β-benzoylethyl)-piperidine (IV). The last compound is an isomer of the normal product III·HCl. The melting points of the hydrochlorides are 125, 175, 145 and 199~200°C, respectively.

$$C_6H_5COCH_3 + HCHO + NH_4Cl \longrightarrow$$

$C_6H_5COCH_2CH_2NH_2 \cdot HCl$ (I·HCl)

$(C_6H_5COCH_2CH_2)_2NH \cdot HCl$ (II·HCl)

$(C_6H_5COCH_2CH_2)_3N \cdot HCl$ (III·HCl)

(IV·HCl)

In general, this cyclic by-product, having a piperidine ring, is obtained by treating compound III·HCl with alkali[2]. It is not considered that compound III·HCl may be converted into the piperidine derivative IV·HCl in the acidic medium which is the usual condition of the Mannich reaction. Therefore, we can regard compounds I·HCl, II·HCl and III·HCl as the normal products in the Mannich reaction, but it is considered plausible that the piperidine derivative IV·HCl may be produced in some different reactions.

Compound II·HCl or III·HCl undergoes decomposition readily when it is heated in the presence of water to give phenyl vinyl ketone[2]. Therefore, at least a small portion of the products in this Mannich reaction will decompose to give phenyl vinyl ketone, because the reaction is carried out in an aqueous medium at 100°C.

$$(C_6H_5COCH_2CH_2)_3N \cdot HCl \xrightarrow{\text{in water}} (C_6H_5COCH_2CH_2)_2NH \cdot HCl + C_6H_5COCH : CH_2$$

(III·HCl) (II·HCl)

It is well known that phenyl vinyl ketone has a great reactivity to amines[4]. So, it is probable that the phenyl vinyl ketone produced may take part in this Mannich reaction.

The reaction of phenyl vinyl ketone with compound II·HCl was carried out, on trial, under the same conditions as those in the Mannich reaction to give a good yield of compound III·HCl and a small quantity of piperidine derivative IV·HCl. During the reaction, however, the temperature was kept at 40~45°C to avoid the polymerization of the phenyl vinyl ketone. This result shows that the above reaction gives the same products as those in the usual Mannich reaction. The same result was obtained, when aqueous alcohol was used instead of water as the medium. Phenyl vinyl ketone also reacted with compound I·HCl to give compound III·HCl and a small quantity of an unknown substance. In this case, piperidine derivative IV·HCl failed to be isolated.

In view of these facts, phenyl vinyl ketone may be thought to have some concern with the main reaction. But phenyl vinyl ketone failed to react with ammonium chloride under the same conditions. At a higher temperature, only the phenyl vinyl ketone polymerized. On the other hand, acetophenone and formaldehyde reacted with compound I·HCl, II·HCl or ammonium chloride to give compound III·HCl and a small quantity of compound IV·HCl.

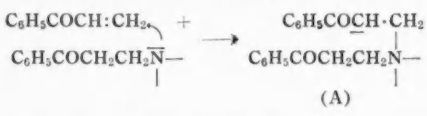
These facts show that the Mannich reaction of acetophenone, formaldehyde and ammonium chloride proceeds step by step to give compounds III·HCl and IV·HCl, and that phenyl vinyl ketone has no concern with the main reaction. But it is thought the phenyl vinyl ketone may have some concern with the side reaction,

1) C. M. van Marle and B. Tollens, *Ber.*, **36**, 1351 (1903); H. Schäfer and B. Tollens, ibid., **39**, 2181 (1906).
2) C. Mannich and S. M. Abdullah, ibid., **68**, 113 (1935).
3) Cf. F. F. Blicke, "Organic Reactions", Vol. 1, John Wiley & Sons, Inc., New York (1942), p. 303; E. R. Alexander and E. J. Underhill, *J. Am. Chem. Soc.*, **71**, 4014 (1949); S. V. Liebermann and E. C. Wagner, *J. Org. Chem.*, **14**, 1001 (1949); K. Bodendorf and G. Koralewski, *Arch. Pharm.*, **271**, 101 (1933).
4) E. P. Kohler, *Am. Chem. J.*, **42**, 375 (1909).

and that the benzoylethyl group of compound I·HCl or II·HCl plays an important role in the reaction with phenyl vinyl ketone.

In the reaction between phenyl vinyl ketone and compound II·HCl, IV·HCl was also obtained as in the Mannich reaction. But it was not probable that this IV·HCl was produced by intramolecular aldol-condensation of compound III·HCl, because compound III·HCl did not undergo isomerization, and gave no piperidine derivative IV·HCl, even when it was heated to 45°C in water. Compound III·HCl was recovered quantitatively after the treatment.

Since compound III·HCl or IV·HCl is stable and does not isomerize, it must be considered that neither of them is the secondary product but the primary one. Thus the mechanism of the reaction may be assumed as follows. The primary step of the reaction is the combination of the β-carbon atom of phenyl vinyl ketone with the nitrogen atom of compound II·HCl.



(A)

The intermediate A catches a proton to give compound III·HCl. When the intermediate A undergoes aldol-condensation intramolecularly, it gives compound IV·HCl. More detailed mechanism will be discussed in later papers.

Experimental

Reaction of Phenyl Vinyl Ketone with Bis-(β-benzoylethyl)-amine Hydrochloride (II·HCl).—A mixture of 1.5 g. of compound II·HCl, 1.5 g. of phenyl vinyl ketone and 15 ml. of water was heated with vigorous stirring at 40~45°C for 1.5 hr. A greater part of compound II·HCl dissolved better in the phenyl vinyl ketone than in water, and a crystalline matter was produced as the reaction proceeded. After being cooled for one hour, the crystals were filtered off, washed with water, and dried; yield, 2.0 g.

The crystals were treated with 8 ml. of alcohol with gentle warming, and the soluble matter was extracted. The insoluble residue (about 0.2 g.) was recrystallized from alcohol, giving compound IV·HCl; m. p. and mixed m. p., 199~201°C[5].

Anal. Found: C, 71.44; H, 6.54; N, 3.07. Calcd. for $C_{27}H_{29}O_3NCl$: C, 72.06; H, 6.27; N, 3.11%.

The alcohol extract was evaporated under reduced pressure, and 1.0 g. of compound III·HCl was obtained; m. p. and mixed m. p., 143~144°C (after drying in vacuo at 78°C).

Anal. Found: C, 72.29; H, 6.20; N, 3.39. Calcd. for $C_{27}H_{29}O_3NCl$: C, 72.06; H, 6.27; N, 3.11%.

The same result was obtained when aqueous alcohol was used in place of water as the medium.

Reaction of Phenyl Vinyl Ketone with Mono-(β-benzoylethyl)-amine Hydrochloride (I·HCl).—A mixture of 2.1 g. of compound I·HCl, 1.5 g. of phenyl vinyl ketone, 5 ml. of water and 5 ml. of alcohol was heated with stirring at 40~45°C for two hours. The mixture was allowed to stand overnight. The crystals produced were filtered off, washed successively with benzene and alcohol-ether mixture, and dried at room temperature; yield, 1.5 g. The crystals were recrystallized from alcohol, giving compound III·HCl; m. p. and mixed m. p., 142~144°C (after drying in vacuo at 78°C).

Anal. Found: C, 71.84; H, 6.55; N, 3.10. Calcd. for $C_{27}H_{29}O_3NCl$: C, 72.06; H, 6.27; N, 3.11%.

The filtrate from compound III·HCl was slightly evaporated to give 0.2 g. of crystals. The crystals were recrystallized from acetone; m. p. 162~164°C. The crystals melted at 174~176°C after repeated recrystallizations. The melting point nearly coincided with that of compound II·HCl (175°C), but the melting point on admixture with an authentic sample depressed exceedingly showing the crystals not to be compound II·HCl. This is further supported by the great solubility of the crystals in alcohol, for the solubility of compound II·HCl is not so great. But it was impossible to make clear whether the crystals were an unknown compound or a mixture of some known compounds, because the yield was too small for the crystals to be identified.

The filtrate from the unknown substance was evaporated under reduced pressure until dry, and 0.5 g. of a residue was obtained. The residue was recrystallized from a mixture of alcohol and acetone; m. p., 121~122°C. The crystals were very soluble in water, and were considered as the starting material I·HCl (m. p., 122~123°C). The melting point on admixture with compound I·HCl did not depress.

Reaction of Bis-(β-benzoylethyl)-amine Hydrochloride (II·HCl) with Acetophenone and Formaldehyde.—A mixture of 3.0 g. of compound II·HCl, 1.2 g. of acetophenone and 1.4 g. of 30% formalin was heated on a steam bath with stirring for 1.5 hr. On cooling, 2.8 g. of crystals were produced. The crystals were filtered off, washed with a mixture of alcohol and ether, and recrystallized from a mixture of alcohol and ether, giving compound III·HCl; m.p. and mixed m. p., 145°C (after drying in vacuo at 78°C).

Anal. Found: C, 71.81; H, 6.18; N, 3.47. Calcd. for $C_{27}H_{29}O_3NCl$: C, 72.06; H, 6.27; N, 3.11%.

The residual mother liquor and washings were concentrated to a syrup under reduced pressure and allowed to stand for about two days to give 0.2 g. of crystals. The crystals were recrystallized from alcohol, giving compound IV·HCl;

5) The melting point of β-benzoylethylamine hydrochloride varies with heating speed because of its instability towards heat.

m. p. and mixed m. p. 199～200°C.

Anal. Found: C, 72.01; H, 6.44; N, 3.03. Calcd. for $C_{27}H_{28}O_3NCl$: C, 72.06; H, 6.27; N, 3.11%.

Reaction of Mono-(β-benzoylethyl)-amine Hydrochloride (I·HCl) with Acetophenone and Formaldehyde.—A mixture of 1.5 g. of compound I·HCl, 2.0 g. of acetophenone and 1.6 g. of 30% formalin was heated on a steam bath with stirring for 1.5 hr. After being cooled for a while, 1.2 g. of crystals were obtained. The crystals were recrystallized from alcohol, giving compound III·HCl; m. p. and mixed m. p., 145°C (after drying in vacuo at 78°C).

Anal. Found: C, 71.41; H, 6.33; N, 3.33. Calcd for $C_{27}H_{28}O_3NCl$: C, 72,06; H, 6.27; N, 3.11%.

The residual mother liquor was allowed to stand for a few days to give 0.1 g. of crystals. The crystals were recrystallized from alcohol, giving compound IV·HCl; m. p. and mixed m. p., 200～201°C.

Anal. Found: C, 70.71; H, 6.32; N, 2.81. Calcd. for $C_{27}H_{28}O_3NCl$: C, 72.06; H, 6.27; N, 3.11%.

Reaction of Phenyl Vinyl Ketone with Ammonium Chloride. — To 10 ml. of water were added 0.25 g. of ammonium chloride and 2.0 g. of phenyl vinyl ketone. The mixture was heated with stirring at 40～45°C for three hours, and was allowed to stand overnight at room temperature to give a resinous matter which was the polymerization product of the phenyl vinyl ketone. The aqueous layer was evaporated until dry under reduced pressure. The residue was confirmed as ammonium chloride by analysis.

Aqueous alcohol (5 : 5 v/v) was used in place of water as the solvent to give the same result. In the case of the higher temperature, the polymerization of phenyl vinyl ketone only was facilitated.

Isomerization of Tris-(β-benzoylethyl)-amine Hydrochloride (III·HCl). — To 7 ml. of water was added 0.5 g. of compound III·HCl, and the mixture was heated with stirring at 45°C for 1.5 hr. On cooling, a crystalline matter was filtered off; yield, 0.5 g. It was recrystallized from alcohol and dried at 78°C in vacuo, giving the starting material III·HCl; m. p., 142～143°C, mixed m. p. on admixture with an authentic sample (143～144°C), 143～144°C.

Summary

1) In the reaction of acetophenone with formaldehyde and ammonium chloride, tris-(β-benzoylethyl)-amine hydrochloride (III·HCl) and 4-hydroxy-4-phenyl-5-benzoyl-1-(β-benzoylethyl)-piperidine hydrochloride (IV·HCl) were produced via bis-(β-benzoylethyl)-amine hydrochloride (II·HCl) after mono-(β-benzoylethyl)-amine hydrochloride (I·HCl).

2) Phenyl vinyl ketone readily reacted with compound I·HCl or II·HCl to give compounds III·HCl and IV·HCl.

The author is particularly indebted to the late Professor Ryuzaburo Nozu and to Professor Ryozo Goto for their discussions and encouragement during this investigation, and also to Professor Seishi Machida for his encouragement.

Chemical Laboratory of Textile Fibres
Kyoto University of Industrial Arts
and Textile Fibres
Kita-ku, Kyoto

Studies on the Mannich Reaction. II. On the Formation of Piperidine Derivatives (2)

By Norito UCHINO

(Received February 19, 1959)

The Mannich reaction of acetophenone with methylamine hydrochloride and formaldehyde gives hydrochlorides of mono-(β-benzoylethyl)-methylamine (V) and bis-(β-benzoylethyl)-methylamine (VI)[1]. The melting points of the hydrochlorides are 139~141°C and 166~169°C, respectively. 4-Hydroxy-4-phenyl-5-benzoyl-1-methyl-piperidine (VII, m. p., 138~140°C) can be obtained by treating compound VI·HCl with alkali, for its isolation is difficult.

$$C_6H_5COCH_3+HCHO+CH_3NH_2\cdot HCl \rightarrow$$

$$C_6H_5COCH_2CH_2NH(CH_3)\cdot HCl \quad (V\cdot HCl)$$

$$(C_6H_5COCH_2CH_2)_2NCH_3\cdot HCl \quad (VI\cdot HCl)$$

$$\begin{matrix} C_6H_5COCHCH_2 \\ \diagdown \quad\quad \diagup \\ C_6H_5C(OH)CH_2CH_2 \end{matrix} NCH_3\cdot HCl \quad (VII\cdot HCl)$$

It has been shown that the reaction of phenyl vinyl ketone with compound V·HCl in aqueous alcohol gives a good yield of VI·HCl together with a small quantity of VII·HCl. When water only was used as the medium, the piperidine base failed to be isolated.

In the reaction of phenyl vinyl ketone with mono-(β-benzoylethyl)-amine hydrochloride (I·HCl), the formation of the isomer of bis-(β-benzoylethyl)-amine hydrochloride (II·HCl) was not certain[2]. But in this case, piperidine derivative VII·HCl could be obtained.

It is necessary to investigate whether or not both of the compounds VI·HCl and VII·HCl were formed at the same time, or whether one of them was formed first and then partly converted into the other. Of course, compound VI·HCl does not isomerize to give compound VII·HCl. Also compound VII·HCl was not converted into compound VI·HCl, under the same conditions as those in the reaction of phenyl vinyl ketone with compound V·HCl.

As the piperidine ring is stable under the above conditions, it is considered that both of the compounds VI·HCl and VII·HCl are primary products of the reaction. The initial step of the reaction may be the combination of the β-carbon atom of phenyl vinyl ketone with the nitrogen atom of compound V·HCl as it has been assumed in the preceding work[2].

If the β-carbon atom of phenyl vinyl ketone can react with the nitrogen atom of β-benzoylethylamine hydrochloride, it seems possible that ammonium chloride or methylamine hydrochloride can also react with phenyl vinyl ketone. Since this is not true, the benzoylethyl group of the amine is likely to play an important role in the reaction.

When a free base of ammonia or methylamine replaced the hydrochloride, it readily reacted with phenyl vinyl ketone to give 4-hydroxy-4-phenyl-5-benzoyl-1-(β-benzoylethyl)-piperidine (IV) or base VII, respectively. The mechanism of this reaction can be considered as follows. The resonance of phenyl vinyl ketone is shown as the following scheme:

$$C_6H_5COCH{:}CH_2 \leftrightarrow C_6H_5C{:}\overset{(+)}{C}HCH_2 \leftrightarrow C_6H_5\overset{(-)}{C}O\overset{(+)}{C}HCH_2$$

$$\underset{(-)}{|\underline{O}|}$$

This positive carbon atom of phenyl vinyl ketone will combine with ammonia or methylamine by attacking the lone pair of electrons of the nitrogen atom, and give tris-(β-benzoylethyl)-amine (III) or base VI, respectively. As a free base III or VI is very unstable, it isomerizes to give piperidine base IV or VII, respectively[1,3].

From the above, it is concluded that phenyl vinyl ketone can react with a nitrogen atom which has a lone pair of electrons. Here, it is also considered that compound I·HCl, II·HCl or V·HCl may react with phenyl vinyl ketone as the free base which is formed by hydrolysis. To show this, it is necessary for β-benzoylethylamines to be weaker bases than

1) C. Mannich and C. Heilner, *Ber.*, **55**, 356 (1922); F. F. Blicke and J. H. Burckhalter, *J. Am. Chem. Soc.*, **64**, 451 (1942); J. T. Plati and W. Wenner, *J. Org. Chem.*, **14**, 543 (1949); cf. C. Mannich and G. Ball, *Arch. Pharm.*, **264**, 65 (1926).

2) N. Uchino, This Bulletin, **32**, 1009 (1959).

3) C. Mannich and S. M. Abdullah, *Ber.*, **68**, 113 (1935).

ammonia or methylamine, and to give sufficient free bases by hydrolysis of the salts. As the free base of β-benzoylethylamines are very unstable, the basicity of them can not be measured directly. Therefore, the dissociation constant was calculated from the hydrogen ion concentration of the aqueous solution of the salt. The hydrogen ion concentration was measured with 0.05 or 0.1 N solution at 20°C.

TABLE I. DEGREE OF HYDROLYSIS OF β-BENZOYLETHYLAMINE HYDROCHLORIDE

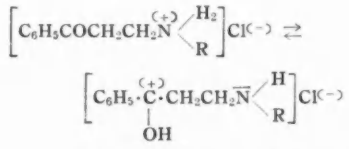
Salt	pH	Dissociation constant of base	Degree of hydrolysis (%)
I·HCl	4.8(0.05 N)	2×10^{-6}	3×10^{-2}
II·HCl	5.0(0.05 N)	5×10^{-6}	2×10^{-2}
V·HCl	5.1(0.1 N)	1×10^{-5}	8×10^{-3}
NH_4Cl		1.79×10^{-5}	
$CH_3NH_2\cdot HCl$		4.38×10^{-4}	

The result of the measurement shows that β-benzoylethylamines are weaker bases than ammonia or methylamine, but their differences are not so great as to elucidate the mechanism of the reaction.

β-Chloropropiophenone was able to react with ammonia to give base IV. As it is well known that phenyl vinyl ketone on being added to hydrogen chloride gives β-chloropropiophenone[4], it may be considered that β-chloropropiophenone is an intermediate product of the reaction. But this consideration is not correct, because it is difficult for ammonium chloride to hydrolyze to give enough hydrochloric acid. In fact, ammonium chloride did not react with phenyl vinyl ketone.

Already it was concluded that (i) the benzoylethyl group plays an important role in the reaction of phenyl vinyl ketone with compound I·HCl, II·HCl or V·HCl, and that (ii) phenyl vinyl ketone can react readily with a nitrogen atom which contains a lone pair of electrons.

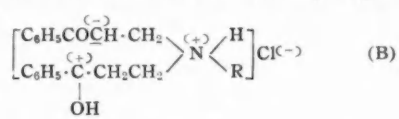
Now, we will assume the following prototropy for β-benzoylethylamine hydrochloride.



R=H, CH_3, $C_6H_5COCH_2CH_2$

4) E. P. Kohler, *Am. Chem. J.*, **42**, 289 (1909).

Here, it is reasonably considered that the β-carbon atom of phenyl vinyl ketone can combine with the lone pair of electrons appearing as in the above equation and gives an intermediate B. The hydrogen



(B)

atom of the hydroxyl group moves to the carbanion as a proton to give the normal product. When the intermediate B undergoes aldol-condensation, it gives the piperidine derivative.

In general, it can be considered that the phenyl vinyl ketone formed by decomposition of the products in the Mannich reaction is concerned with the formation of the piperidine bases which are found in that reaction.

Experimental

Reaction of Mono-(β-benzoylethyl)-methylamine Hydrochloride (V·HCl) with Phenyl Vinyl Ketone.—To a mixture of 5 ml. of water and 3 ml. of alcohol were added 0.5 g. of phenyl vinyl ketone and 0.5 g. of compound V·HCl. The mixture was next heated with stirring at 45~50°C for 2.5 hr. Then the mixture was evaporated until dry under reduced pressure, and washed with benzene to remove the polymerized phenyl vinyl ketone. The residue obtained (0.9 g.) was extracted with a small volume of water, and the insoluble matter (0.8 g.) was recrystallized from alcohol giving compound VI·HCl; m.p. and mixed m.p., 165~167°C.

Anal. Found: C, 68.70; H, 6.83; N, 4.16. Calcd. for $C_{19}H_{22}O_2NCl$: C, 68.76; H, 6.68; N, 4.22%.

The extract was evaporated under reduced pressure. The extraction and evaporation were repeated once more, and the solid matter obtained was recrystallized twice from alcohol giving 0.05 g. of compound VII·HCl; m.p. and mixed m.p., 196~198°C.

Anal. Found: C, 68.71; H, 6.79; N, 4.11. Calcd. for $C_{19}H_{22}O_2NCl$: C, 68.76; H, 6.68; N, 4.22%.

Isomerization of 4-Hydroxy-4-phenyl-5-benzoyl-1-methyl-piperidine Hydrochloride (VII·HCl).—In 5 ml. of water was dissolved 0.2 g. of compound VII·HCl, and the solution was heated to 40~45°C for 1.5 hr. If compound VI·HCl is formed by isomerization, some crystalline matter is expected to appear because of its small solubility. But no crystalline matter appeared. The same result was obtained not only when the temperature of the reaction was kept at 55~60°C, but also when three drops of concentrated hydrochloric acid or a small quantity of alkali was added to the solution, respectively. Removal of the solvent

under reduced pressure gave the starting material VII·HCl; m. p. and mixed m. p., 196~198°C.

Reaction of Phenyl Vinyl Ketone with Methylamine Hydrochloride.—Two grams of methylamine hydrochloride were dissolved in 3 ml. of water, and about 1 g. of phenyl vinyl ketone was added to the solution. The solution was heated with stirring at 50~55°C for five hours. Almost all the phenyl vinyl ketone polymerized. The aqueous solution was evaporated until dry under reduced pressure. The residue was confirmed to be only methylamine hydrochloride, and no β-benzoylethylamine hydrochloride was detected.

Reaction of Phenyl Vinyl Ketone with Ammonia.—A mixture of 1 g. of phenyl vinyl ketone, 0.5 ml. of aqueous ammonia (28%) and 10 ml. of water was heated with shaking at 40°C for two minutes. The greater part of the phenyl vinyl ketone polymerized to become viscous, and the liquid phase became turbid. After standing overnight at room temperature, the crystals produced were picked up with a pincette, and were washed with alcohol. As it was difficult to separate the crystals from the resinous matter, the yield was only 0.1 g. The crystals were recrystallized from alcohol, giving base IV; m. p. and mixed m. p., 147~148°C.

Anal. Found: C, 77.90; H, 6.52; N, 3.73. Calcd. for $C_{27}H_{27}O_3N$: C, 78.42; H, 6.58; N, 3.38%.

Reaction of Phenyl Vinyl Ketone with Methylamine.—A gas of excessive methylamine was passed into a solution of 4.5 g. of phenyl vinyl ketone in ether with ice cooling. Then the solution was evaporated to a syrup, which solidified after a while; yield, 4.7 g. The product was recrystallized from methanol giving 2.0 g. of base VII; m. p. and mixed. m. p., 139~140°C.

Anal. Found: C, 77.20; H, 7.25; N, 4.73. Calcd. for $C_{19}H_{21}O_2N$: C, 77.25; H, 7.16; N, 4.74%.

Reaction of β-Chloropropiophenone with Ammonia.—To a solution of 5 ml. of water and 5 ml. of alcohol were added 1 g. of β-chloropropiophenone and 1 ml. of aqueous ammonia (25%), and the mixture was heated with stirring at 40~45°C for an hour. One gram of a crystalline substance was formed. On cooling, the crystals were filtered off and recrystallized from alcohol giving base IV; m. p. and mixed m. p., 148~149°C.

Anal. Found: C, 78.48; H, 6.62; N, 3.63. Calcd. for $C_{27}H_{27}O_3N$: C, 78.42; H, 6.58; N, 3.38%.

β-Chloropropiophenone could react with ammonia, but not with ammonium chloride.

Summary

1) The mechanism of the reaction of phenyl vinyl ketone with β-benzoylethylamine hydrochloride was discussed.

It was concluded that the β-carbon atom of phenyl vinyl ketone combined with β-benzoylethylamine hydrochloride on attacking the lone pair of electrons which appeared in consequence of prototropy, and gave the same products as those in the Mannich reaction.

2) In the Mannich reaction, piperidine bases are found to be produced.

It was concluded that the phenyl vinyl ketone, which was produced by decomposition of the products in the Mannich reaction, was concerned with the formation of these piperidine bases.

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Chemical Laboratory of Textile Fibres
Kyoto University of Industrial Arts
and Textile Fibres
Kita-ku, Kyoto

Localization Energy with Electronic Interaction

By Kenichi FUKUI, Keiji MOROKUMA and Teijiro YONEZAWA

(Received January 30, 1959)

The localization method by Wheland[1], in which localization energy is employed as the reactivity index, has achieved successes in interpreting chemical reactivity of conjugated molecules[2]. On the other hand, total π-electron density[3], self-polarizability[4], free valence[5], frontier electron density[6] and superdelocalizability[7] are introduced as good reactivity indexes in the approximation of the simple LCAO treatment. Regarding alternant hydrocarbons (AH's) some mathematical relations have been found between localization energy and other reactivity indexes[8].

In the previous paper[9], utilizing LCAO SCF wave function, namely, the wave function where electronic interaction is explicitly included, we have found that the total π-electron density can not predict the correct reactivity of molecules, while the frontier electron density remains a good index for both ionic and radical reactions in LCAO SCF MO treatment just as well as in usual simple LCAO MO treatment. In the present paper we have defined and calculated the localization energy under an explicit consideration of electronic interaction, and comparison of the results obtained by the present method with those in simple LCAO treatment has been made.

Theoretical

Model of Localized System.—According to Wheland's definition the localized system in the transition state has the configuration in which the attacked carbon atom is sp^3-hybridized, so that the resonance integrals between the attacked atom and the neighboring ones are taken to be zero. More precisely the integral does not completely vanish; however, in order to be faithful to the concept of the term "localization", we assume that the resonance integrals between the attacked atom and the others are always zero. This assumption may be reasonable for our approximate calculation.

Here one more problem arises: Simple treatment naturally allows us to deal with the two parts, the localized electrons and the residue, independently from each other; but when we want to take the electronic interaction into account, the interaction between the two parts, and that between those two and the attacking reagent must be considered, as well as the mutual interaction of electrons inside the residue*. Concerning this point, two approximations would be employed. As the first approximation (Approx. 1) we simply assume the two parts to be independent, that is, the only electronic interaction to be taken into account is that which acts inside the residue*. In the second approximation (Approx. 2) the interaction between the two parts shall be treated as a perturbation. The effects of attacking reagent, which do not seem essential to the localization method, are thoroughly neglected for simplicity in both approximations.

Formulation.—The wave function χ_0 of the "isolated" system consisting of $2n$ carbon atoms and $2n$ π-electrons is given as follows:

$$\chi_0 = \frac{1}{\sqrt{(2n)!}} \begin{vmatrix} (\psi_1\alpha)^1 (\psi_1\beta)^1 (\psi_2\alpha)^1 & \cdots\cdots & (\psi_n\beta)^1 \\ (\psi_1\alpha)^2 (\psi_1\beta)^2 (\psi_2\alpha)^2 & \cdots\cdots & (\psi_n\beta)^2 \\ \cdots\cdots & \cdots\cdots & \cdots\cdots \\ \cdots\cdots & \cdots\cdots & \cdots\cdots \\ (\psi_1\alpha)^{2n} (\psi_1\beta)^{2n} (\psi_2\alpha)^{2n} \cdots\cdots & & (\psi_n\beta)^{2n} \end{vmatrix}$$

$$\equiv (1/\sqrt{(2n)!}) \left[(\psi_1\alpha)^1 (\psi_1\beta)^2 (\psi_2\alpha)^3 \cdots\cdots (\psi_n\beta)^{2n} \right] \quad (1)$$

* In electrophilic reaction, the interaction between the two localized electrons is also to be included.

1) G. W. Wheland, *J. Am. Chem. Soc.*, **64**, 900 (1940).
2) M. J. S. Dewar, *J. Chem. Soc.*, **1952**, 691; H. C. Longuet-Higgins, *J. Chem. Phys.*, **18**, 283 (1950); T. Yonezawa et al., *Chem. High Polymers* (*Kobunshi Kagaku*), **14**, 533 (1957).
3) G. W. Wheland and L. Pauling, *J. Chem. Phys.*, **1**, 606 (1933); etc.
4) C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc.* (*London*), **A191**, 39 (1947); **A192**, 16 (1947).
5) F. H. Burkitt et al., *Trans. Faraday Soc.*, **47**, 553 (1951).
6) K. Fukui, T. Yonezawa and H. Shingu, *J. Chem. Phys.*, **20**, 722 (1952); etc.
7) K. Fukui, T. Yonezawa and C. Nagata, This Bulletin, **27**, 423 (1954).
8) K. Fukui, T. Yonezawa and C. Nagata, *J. Chem. Phys.*, **26**, 831 (1957); H. Baba, This Bulletin, **30**, 147, 154, (1957).
9) K. Fukui, K. Morokuma and T. Yonezawa, This Bulletin, **32**, 853 (1959).

where φ_i is the i-th MO, α and β are the spin functions, and the superscripts denote the numbering of electrons. Each MO should be chosen to minimize the electron energy of the system; but so far as the evaluation of localization energy with electronic interaction is concerned, it seems sufficient to use Hückel MO

$$\psi_i=\sum_\mu c_{i\mu}\phi_\mu \qquad (i=1,2,\cdots\cdots,2n) \tag{2}$$

where ϕ_μ denotes the AO on the μ-th carbon atom.

Introducing a SCF-like procedure proposed by Pople[10], we obtain the following expression of the total electronic energy of the system**.

$$\varepsilon_0=2nU+(\gamma_{\mu\mu}/4)\sum_\mu (P_{\mu\mu})^2+2\beta\sum_{\mu<\nu}{}^{*} P_{\mu\nu} +\sum_{\mu<\nu}\{(P_{\mu\mu}-1)(P_{\nu\nu}-1)-(1/2)(P_{\mu\nu})^2\}\gamma_{\mu\nu} \tag{3}$$

where U is a core matrix element and is put a constant, β is the resonance integral between the nearest neighbors, and $\gamma_{\mu\nu}$ is the coulomb repulsion integral

$$\gamma_{\mu\nu}=\int\phi_\mu^*(1)\phi_\nu^*(2)\frac{e^2}{r_{12}}\phi_\mu(1)\phi_\nu(2)\mathrm{d}v_1\mathrm{d}v_2 \tag{4}$$

and

$$P_{\mu\nu}=2\sum_{i=1}^{n} c_{i\mu}c_{i\nu} \tag{5}$$

Summation Σ and Σ^* should cover all the atoms and the nearest neighboring atoms, respectively. In deriving Eq. 3 the same assumptions as proposed by Pople[10], for instance, of equi-bond-length, of neglecting the coulomb penetration integrals and so on, are employed.

From the assumption made in the preceding section the wave function χ_E of the "localized" system (transition complex) for electrophilic reaction, in which two electrons are localized on the carbon λ, may be written as follows:

$$\chi_E=(1/\sqrt{(2n-2)!})[(\psi'_1\alpha)^1(\psi'_1\beta)^2\cdots\cdots \times(\varphi'_{n-1}\alpha)^{2n-3}(\psi'_{n-1}\beta)^{2n-2}] \times(1/\sqrt{2!})[(\phi_\lambda\alpha)^{2n-1}(\phi_\lambda\beta)^{2n}] \tag{6}$$

where ψ'_i is the i-th Hückel MO for the residue consisting of $(2n-1)$ carbons.

$$\psi'_i=\sum_\mu c'_{i\mu}\phi_\mu \quad (i=1,2,\cdots\cdots,2n-1) \tag{7}$$

Here we refer the superscript "$'$" to the residue of the molecule. The two parts being treated separately (Approx. 1), the energy of the system, ε_{E0}, is given as follows[11]:

$$\varepsilon_{E0}=2U+\gamma_{\mu\mu}+(2n-2)U+(\gamma_{\mu\mu}/4)\sum_\mu (P^+{}_{\mu\mu})^2 +2\beta\sum_{\mu<\nu}{}^{*} P^+{}_{\mu\nu}+\sum_{\mu<\nu}\{(P^+{}_{\mu\mu}-1)(P^+{}_{\nu\nu}-1) -(1/2)(P^+{}_{\mu\nu})^2\}\gamma_{\mu\nu} \tag{8}$$

where

$$P^+{}_{\mu\nu}=2\sum_{i=1}^{n-1} c'_{i\mu}c'_{i\nu} \tag{9}$$

The first two terms correspond to the energy of the localized electrons and the others to that of the residue. When the interaction between the parts is taken into account in higher approximation (Approx. 2), the interaction energy ε_{E1}:

$$\varepsilon_{E1}=\sum_\mu (P^+{}_{\mu\mu}-1)\gamma_{\mu\lambda} \tag{10}$$

is to be added to the energy ε_{E0}.

Also for nucleophilic reaction, through the similar consideration as for electrophilic one, we easily obtain the following formulae.

$$\chi_N=(1/\sqrt{(2n)!})[(\psi'_1\alpha)^1(\psi'_1\beta)^2\cdots\cdots \times(\psi'_n\alpha)^{2n-1}(\psi'_n\beta)^{2n}] \tag{11}$$

$$\varepsilon_{N0}=2nU+(\gamma_{\mu\mu}/4)\sum_\mu (P^-{}_{\mu\mu})^2 +2\beta\sum_{\mu<\nu}{}^{*} P^-{}_{\mu\nu}+\sum_{\mu<\nu}\{(P^-{}_{\mu\mu}-1) \times(P^-{}_{\nu\nu}-1)-(1/2)(P^-{}_{\mu\nu})^2\}\gamma_{\mu\nu} \tag{12}$$

$$\varepsilon_{N1}=\sum_\mu (1-P^-{}_{\mu\mu})\gamma_{\mu\lambda} \tag{13}$$

$$P^-{}_{\mu\nu}=2\sum_{i=1}^{n} c'_{i\mu}c'_{i\nu} \tag{14}$$

For radical reaction,

$$\chi_R=(1/\sqrt{(2n-1)!})[(\psi'_1\alpha)^1(\psi'_1\beta)^2\cdots\cdots \times(\psi'_{n-1}\alpha)^{2n-3}(\psi'_{n-1}\beta)^{2n-2} \times(\psi'_n\alpha)^{2n-1}]\cdot(\phi_\lambda\alpha)^{2n} \tag{15}$$

$$\varepsilon_{R0}=U+(2n-1)U+\gamma_{\mu\mu}+\sum_\mu P^\alpha{}_{\mu\mu}P^\beta{}_{\mu\mu} +2\beta\sum_{\mu<\nu}{}^{*} P^0{}_{\mu\nu}+\sum_{\mu<\nu}\{(P^0{}_{\mu\mu}-1)(P^0{}_{\nu\nu}-1) -[(P^\alpha{}_{\mu\nu})^2+(P^\beta{}_{\mu\nu})^2]\}\gamma_{\mu\nu} \tag{16}$$

$$\varepsilon_{R1}=0 \tag{17}$$

$$P^\alpha{}_{\mu\nu}=\sum_{i=1}^{n} c'_{i\mu}c'_{i\nu}=(1/2)P^-{}_{\mu\nu}$$
$$P^\beta{}_{\mu\nu}=\sum_{i=1}^{n-1} c'_{i\mu}c'_{i\nu}=(1/2)P^+{}_{\mu\nu} \tag{18}$$
$$P^0{}_{\mu\nu}=P^\alpha{}_{\mu\nu}+P^\beta{}_{\mu\nu}$$

10) J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953).

** Core-core repulsion energies are included in all the expressions of energies in this paper.

11) A. Brickstock and J. A. Pople, *Trans. Faraday Soc.*, **50**, 901 (1954).

TABLE I. LOCALIZATION ENERGIES OF ALTERNANT HYDROCARBONS

Compound	Position	Ionic ($L_N=L_E$)[a] Approx. 1	Ionic ($L_N=L_E$)[a] Approx. 2	Radical (L_R)[a] Approxs. 1 & 2	Simple[b] ($L_N=L_E=L_R$)
Ethylene	—	13.695	6.395	3.165	2.000
Butadiene (*trans*)	1	11.854	6.324	2.590	1.694
	2	14.467	7.167	3.937	2.472
Benzene	—	13.834	7.334	4.995	2.536
Naphthalene	1	12.918	7.134	4.411	2.299
	2	13.470	7.473	4.888	2.480
Anthracene	1	12.575	7.160	4.255	2.240
	2	13.233	7.676	4.755	2.423
	9	11.806	6.882	3.636	2.013
Phenanthrene	1	12.821	7.212	4.604	2.317
	9	12.872	7.147	4.361	2.297
Biphenyl	2	13.157	7.191	4.905	2.400
	4	13.196	7.483	4.944	2.447

a) In units of eV.
b) In units of $(-\beta)$.

TABLE II. LOCALIZATION ENERGIES OF NON-ALTERNANT HYDROCARBONS

Compound	Position	Electrophilic (L_E) Approx. 1[a]	Electrophilic (L_E) Approx. 2[a]	Electrophilic (L_E) Simple[b]	Nucleophilic (L_N) Approx. 1[a]	Nucleophilic (L_N) Approx. 2[a]	Nucleophilic (L_N) Simple[b]	Radical (L_R) Approxs. 1 & 2[a]	Radical (L_R) Simple[b]
Azulene	1	11.392	6.543	1.352	13.265	7.572	2.090	4.177	1.721
	2	12.521	8.100	1.728	12.734	6.694	1.728	4.500	1.728
	4	13.760	8.148	1.808	10.559	5.280	1.231	3.987	1.520
	5	12.654	6.655	1.659	12.595	8.274	1.655	4.485	1.655
	6	13.755	7.349	1.959	11.177	8.959	1.280	4.368	1.620
Fulvalene	1	12.908	5.969	1.987	9.408	5.145	1.365	3.021	1.676
	2	13.702	6.680	2.236	10.507	7.131	1.452	3.783	1.848

a) In units of eV.
b) In units of $(-\beta)$.

The first term in Eq. 16 refers to the localized electron and the others to the residue.

As regards the AH, whose MO has special simplifying properties, Eqs. 8, 10, 12, 13 and 16 can be reduced to simpler ones, that is,

$$\varepsilon_{N0}=\varepsilon_{E0}=2nU+(\gamma_{\mu\mu}/4)\,[(n-1)+\sum_{\mu\nu}^{st}\{1+(c'_{n\mu})^2\}^2]+2\beta\sum_{\mu<\nu}^{*}P^0_{\mu\nu}-\{-\sum_{\mu<\nu}^{st,\,st}(c'_{n\mu}c'_{n\nu})^2+\sum_{\mu,\nu}^{st,unst}(P^0_{\mu\nu})^2\}(\gamma_{\mu\nu}/2) \tag{19}$$

$$\varepsilon_{N1}=\varepsilon_{E1}=-\sum_{\mu}^{st}(c'_{n\mu})^2\gamma_{\mu\lambda} \tag{20}$$

$$\varepsilon_{R0}=2nU+(\gamma_{\mu\mu}/4)\{(2n-1)-\sum_{\mu}^{st}(c'_{n\mu})^4\}+2\beta\sum_{\mu<\nu}^{*}P^0_{\mu\nu}-\{\sum_{\mu<\nu}^{st,\,st}(c'_{n\mu}c'_{n\nu})^2+\sum_{\mu,\nu}^{st,\,unst}(P^0_{\mu\nu})^2\}(\gamma_{\mu\nu}/2) \tag{21}$$

Summation $\sum^{st}$ and $\sum^{unst}$ should cover all the starred and the unstarred atoms, respectively.

The localization energies, L, of the λ-th carbon atom are, therefore, obtained from the following equations.

$$\begin{aligned}&\text{Electrophilic Reaction}\\&\quad\text{(Approx. 1)}\qquad L_E=\varepsilon_{E0}-\varepsilon_0\\&\quad\text{(Approx. 2)}\qquad L_E=\varepsilon_{E0}+\varepsilon_{E1}-\varepsilon_0\\&\text{Nucleophilic Reaction}\\&\quad\text{(Approx. 1)}\qquad L_N=\varepsilon_{N0}-\varepsilon_0\\&\quad\text{(Approx. 2)}\qquad L_N=\varepsilon_{N0}+\varepsilon_{N1}-\varepsilon_0\\&\text{Radical Reaction}\\&\quad\text{(Approxs. 1 \& 2)}\ L_R=\varepsilon_{R0}+\varepsilon_0\end{aligned} \tag{22}$$

Evaluation of Atomic Integrals. — For numerical evaluation of β and $\gamma_{\mu\nu}$ are utilized the semi-empirical formulae introduced by Pariser and Parr[12]. For simplicity, as partly stated above, all the

12) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 767 (1953).

C-C bond distances are assumed the same, 1.39Å, and all the carbon rings (five- and seven-membered rings for azulene and fulvalene, six-membered rings for the other molecules now considered) are supposed to be regular, and polyenyl bond angles to be 120°.

Results and Discussion

The calculated results of localization energy, which is defined in the preceding section, of seven AH's and two non-AH's are listed in Tables I and II***, together with those obtained by simple LCAO treatment.

As is seen from Eq. 20, the interaction energy between the localized electrons and the residue in nucleophilic and in electrophilic reactions is necessarily negative for the AH, namely, there rises some stabilization of the system from the interaction, this seeming true also for the non-AH (cf. Eqs. 10 and 13); and accordingly the values of the localization energies, L_E and L_N, in Approx. 1 are larger than in Approx. 2. For all that we can see in Tables I and II that in both approximations we obtain nearly the same intramolecular orientation, which will be discussed in the later paragraph in detail. In radical reaction, on the other hand, the interaction energy formally vanishes (cf. Eq. 17), and therefore both approximations give the same value of localization energy.

It will be seen in Tables I and II that the magnitude of L_R is generally much smaller than those of L_N and L_E in both approximations, whereas in the simple LCAO treatment the magnitude of L_R lies between those of L_N and L_E. This by no means admits that the activation energy of radical reaction is smaller than those of the others, because effects of reagents and changes in the σ-system are conventionally set aside from this argument. Especially for the AH Eqs. 19 and 20 show the relation $L_E = L_N$ within each approximation in accordance with the result obtained by the simple treatment.

It may be valuable to notice that both approximations indicate the same intramolecular orientation as the simple treatment for all the reactions of the molecules now concerned, except for the ionic reactions of phenanthrene in Approx. 1. Accordingly, its agreement with experimental results is mostly good, but the facts that azulene reacts at the position 1 in radical reaction[13] (L_R is the smallest at 4) and that the position 4 of biphenyl is more reactive than the position 2 both in radical and electrophilic reactions[14] (L_R and L_E indicate 2-orientation) can not be explained on the basis of the localization energy, whether the electronic interaction is taken into account or not. In fulvalene the position 1 is shown to be the most susceptible to attack by localization energies and the position 2 is so by frontier electron density[15], superdelocalizability[16] and total π-electron density[17],

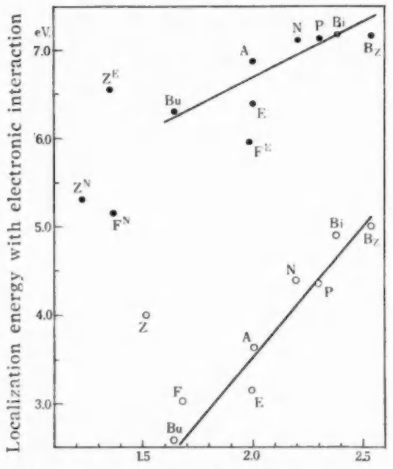


Fig. 1. Relationship between localization energies in simple treatment and with electronic interaction.
○: Radical reaction, ●: Ionic reaction (Approx. 2); E: ethylene, Bu: butadiene, Bz: benzene, N: naphthalene, A: anthracene, P: phenanthrene, F: fulvalene (F^N: nucleophilic, F^E: electrophilic), Z: azulene (Z^N: nucleophilic, Z^E: electrophilic). Only the position of the smallest localization energy of each molecule is plotted. The straight lines are only for AH's.

*** For the position 2 of butadiene, the wave functions of the localized system are expressed in the product of wave functions of three parts, as follows:

$$\chi_E = (1/\sqrt{2})[(\varphi_1'\alpha)^1(\varphi_1'\beta)^2] \times (1/\sqrt{2})[(\phi_2\alpha)^3(\phi_2\beta)^4]$$
$$\chi_R = (1/\sqrt{2})[(\varphi_1'\alpha)^1(\varphi_1'\beta)^2]\cdot(\phi_2\alpha)^3\cdot(\phi_1\alpha)^4$$
$$\chi_N = (1/\sqrt{2})[(\varphi_1'\alpha)^1(\varphi_1'\beta)^2] \times (1/\sqrt{2})[(\phi_1\alpha)^3(\phi_1\beta)^4]$$

In Approx. 1 three parts are treated independently, whereas their mutual interactions are taken into account in Approx. 2.

13) H. Arnold and K. Pahls, *Chem. Ber.*, **89**, 121 (1956).
14) G. Schults, H. Schmidt and H. Strasser, *Ann.*, **207**, 352 (1881); etc.
15) To be published.
16) To be published.
17) R. D. Brown, *Trans. Faraday Soc.*, **45**, 296 (1949).

further experiments being awaited at this point.

It seems also interesting that, except for the mutual coincidence of the most reactive position, the order of reactivity of each position in azulene does not coincide with one another in the three treatments; in electrophilic reaction, for instance, the reactivity of each position decreases in the order $1>5>2>4>6$ in the simple treatment, $1>2>5>6>4$ in Approx. 1, and $1>5>6>2>4$ in Approx. 2.

As it is seen in Fig. 1, agreement of the intermolecular order of reactivity predicted by the simple treatment with that obtained with electronic interaction is not so good in Approx. 2; and in Approx. 1 the agreement is a little worse. Non-AH's, azulene and fulvalene, largely deviate from the linear relationship of Fig. 1, but unfortunately there are no available data to check which result is correct.

From the above discussion it might be concluded that the localization energy, in which the electronic interaction is taken into account, can be a pretty good index of chemical reactivity.

Department of Fuel Chemistry
Faculty of Engineering
Kyoto University
Sakyo-ku, Kyoto

Added in Proof:

It is easily proved that the following wave functions χ'_E and χ'_R, instead of Eqs. 6 and 15, directly lead to the same energy expressions that were derived in Approx. 2, ε'_E and ε'_R respectively.

$$\chi'_E=(1/\sqrt{(2n)!})[(\phi'_1\alpha)^1(\phi'_1\beta)^2\cdots(\phi'_{n-1}\alpha)^{2n-3}\times(\phi'_{n-1}\beta)^{2n-2}(\phi_2\alpha)^{2n-1}(\phi_2\beta)^{2n}]$$

$$\varepsilon'_E=\varepsilon_{E0}+\varepsilon_{E1}$$

$$\chi'_R=(1/\sqrt{(2n)!})[(\phi'_1\alpha)^1(\phi'_1\beta)^2\cdots(\phi'_{n-1}\alpha)^{2n-3}\times(\phi'_{n-1}\beta)^{2n-2}(1/\sqrt{2})\times\{(\phi'_n\alpha)^{2n-1}(\phi_2\beta)^{2n}-(\phi'_n\beta)^{2n-1}(\phi_2\alpha)^{2n}\}]$$

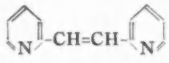
$$\varepsilon_R'=\varepsilon_{R0}$$

Geometrical Isomers of 1,2-Bis-(2-pyridyl)-ethylene

By Takumi KATSUMOTO

(Received February 5, 1959)

1,2-Bis-(2-pyridyl)-ethylene (I) is expected to exhibit geometrical isomerism and to exist in a *cis*- and a *trans*-form. Hitherto, however, only one species has been known. It was first synthesized by Lénárt[1] and melted at 118~119°C. But it has been unknown to which form it belongs. The present author has prepared the other form and concluded from physical properties that the former is the *trans*-isomer and the latter is the *cis*-isomer.



(I)

Experimental

Synthesis of 1,2-Bis-(2-pyridyl)-ethylene. — It was prepared from 2-pyridylformaldehyde, α-picoline and anhydrous zinc chloride. 2-Pyridylformaldehyde, obtained from the Wako Co., was distilled under reduced pressure and the fraction boiling at 76~77°C/17 mmHg was used. α-Picoline, obtained from the Eastman Kodak, was fractionated in an efficient column (b. p., 129.3°C).

A mixture of 2-pyridylformaldehyde (2 g.), α-picoline (3 g.) and anhydrous zinc chloride (2 g.) was heated in a sealed tube at 200°C for 24 hr. After being cooled, the dark brown viscid product was dissolved in aqueous hydrochloric acid. The acid solution was then basified with sodium hydroxide and steam-distilled to remove the unchanged α-picoline. The black oil, which separated on the surface of the solution, was extracted with chloroform and the chloroform extract was dried over anhydrous sodium sulfate and evaporated. The resinous residue was distilled under reduced pressure in a Claisen flask fitted with a wide saber-shaped side tube. A deeply yellow oil distilled out over the interval 150~220°C /15 mmHg and condensed in the side tube. The distillate was extracted with boiling ether, and evaporation of the extract gave 1,2-bis-(2-pyridyl)-ethylene as a brown sticky oil.

Separation of Two Isomers.—The isomers were

1) C. H. Lénárt, *Ann.*, 410, 95 (1915).

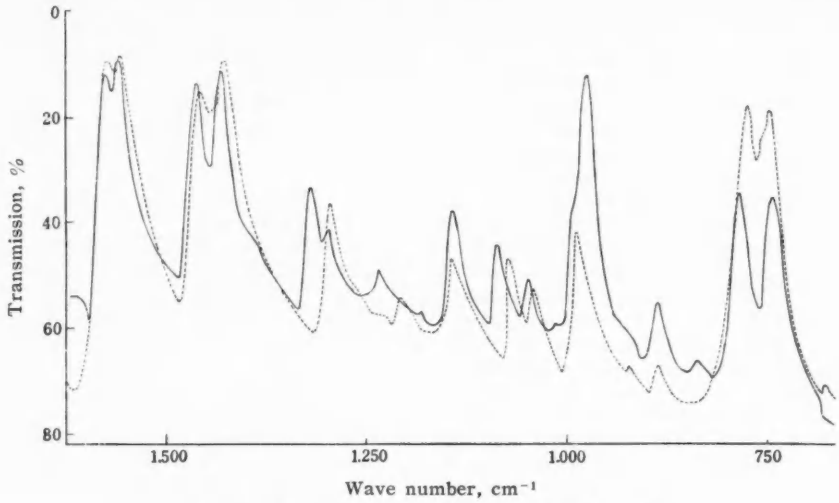


Fig. 1. Infrared spectra of 1,2-bis-(2-pyridyl)-ethylene.
—— compound II (*trans*), ------ compound III (*cis*)

separated by the elution chromatography. The oil was dissolved in chloroform, dried with calcium chloride, and chromatographed on a column (2×13 cm.) of alumina and the column was eluted with the same solvent to give pale brown crystals melting at 70~105°C. Two additional chromatographs on alumina column (2×41 cm.; chloroform) separated them into two parts. One (II), eluted first, forms colorless prisms, m.p. 120~121°C, and corresponds to the compound described by Lénárt. The other (III), contained in the next elute, forms colorless needles and melts sharply at 48.0~48.5°C.

Measurements of Physical Properties. — The boiling points at 15 mmHg pressure were measured by Garcia's method[2]. The pressure was kept constant with a mercury pressure controller fitted with a large buffer bottle (sensitivity, ±0.5 mmHg).

The ultraviolet absorption spectra in cyclohexane were measured with a Shimadzu spectrophotometer. The wavelength of the photometer was calibrated with the absorption band at 301 mμ of an aqueous potassium nitrate solution[3-5]. The infrared spectra in potassium bromide disks were obtained with a Hilger double beam spectrophotometer.

Results and Discussion

The results of the elementary analyses of the two species, II and III, are just the same and consistent with the formula, $C_{12}H_{10}N_2$ (Table I), thus showing that they are isomers.

TABLE I. COMPARISON OF THE TWO ISOMERS OF 1,2-BIS-(2-PYRIDYL)-ETHYLENE

	Compound II	Compound III
Elementary analysis		
Found	C: 78.97% H: 5.738 N: 15.42	C: 78.79% H: 5.729 N: 15.49
Calcd. for $C_{12}H_{10}N_2$	C: 79.09% H: 5.53 N: 15.38	
m. p.	120.0~121.0°C	48.0~48.5°C
b. p.	197.0°C	148.5°C
Configuration	*trans*	*cis*

The infrared spectra of the two isomers, II and III, are given in Fig. 1. All bands of II correspond to those of III, except two strong bands located at 968 and 1318 cm^{-1} as shown in Table II. The band at 986 cm^{-1} of III is not clearly noticed in the spectrum of II, but it seems to be hidden by the very strong band at 968 cm^{-1}, because a shoulder is found in this region. Lunde and Zechmeister[6] also found the absorption band at 980 cm^{-1} as a shoulder on the adjacent and intense band at 960 cm^{-1} in the spectra of many *trans*-diphenylpolyenes including *trans*-stilbene.

A number of the common absorption

2) C. R. Garcia, *Ind. Eng. Chem., Anal. Ed.*, **15**, 648 (1943).
3) D. T. Ewing et al., ibid., **12**, 639 (1940).
4) J. M. Vandenbelt et al., ibid., **17**, 235 (1945).
5) H. Ley and F. Volbert, *Z. phisik. Chem.*, **130**, 308 (1927).
6) K. Lunde and L. Zechmeister, *Acta Chem. Scand.*, **8**, 1421 (1954).

TABLE II. INFRARED ABSORPTION BANDS OF 1,2-BIS-(2-PYRIDYL)-ETHYLENE

Compound II $\tilde{\nu}_{max}$ (cm^{-1})	Compound III $\tilde{\nu}_{max}$ (cm^{-1})	Assignment**
738 (vs)*	746 (vvs)*	Py-1
780 (vs)	778 (vvs)	Py-1
883 (m)	885 (w)	
968 (vvs)		E
(986 s)	986 (s)	Py-2
1045 (w)	1045 (w)	Py-2
1083 (m)	1073 (m)	Py-2
1138 (s)	1149 (m)	Py-2
1295 (w)	1299 (s)	
1318 (s)		
1428 (vvs)	1430 (vvs)	Py-2
1460 (vvs)	1460 (vs)	Py-3
1559 (vvs)	1561 (vvs)	Py-3
1574 (m)	1578 (s)	Py-3

* The letters shown in the brackets mean the relative intensities. v=very, s=strong, m=medium and w=weak.

** Py-1,2,3 mean the CH out-of-plane deformation, the CH in-plane deformation, and the ring stretching vibration of 2-substituted pyridine ring, respectively. E means the CH out-of-plane deformation of -CH=CH- (*trans*).

bands show that these two compounds have very similar structures. These bands are assigned to the vibrations arising from the 2-substituted pyridine ring as follows:

The infrared spectra of substituted pyridines are closely similar to those of substituted benzenes, although the effect of the electronegative nitrogen appears regularly. All substituted pyridines exhibit strong and characteristic absorptions in the regions 700~850 cm^{-1} due to the out-of-plane bending vibrations of the ring CH. Shindo[7] suggested that 2-substituted pyridines show intense absorptions in the regions 740~780 cm^{-1}, while 3-derivatives do in the regions 770~820 cm^{-1} (m-s) and 690~730 cm^{-1} (vs), and 4-derivatives in the region 790~850 cm^{-1} (s). The 738 cm^{-1} band of II and the 746 cm^{-1} of III suggest that these compounds are 2-derivatives.

Bellamy[8] suggested that a series of weak absorptions in the regions 990~1200 cm^{-1} shown by substituted benzenes are peculiar to the types of substitution. Randall et al.[9] also found that the absorption near 1020 cm^{-1} in monosubstituted benzenes are independent of the nature of the substituent and assigned it to the in-plane bending vibration of CH. Shindo[7] suggested that a series of weak but sharp absorptions in this region are also found in the case of monosubstituted pyridines and the positions are almost constant regardless of the nature of the substituent and that three absorption bands in the regions 988~998 cm^{-1}, 1041~1050 cm^{-1} and 1140~1151 cm^{-1} are characteristic of 2-substituted pyridines. He also attributed them to the in-plane bending mode of the ring involving a considerable ring vibration. Of the four common bands in the spectra of the present compounds, three bands at 986, 1045 and 1138 cm^{-1} of II and those at 986, 1045 and 1149 cm^{-1} of III are respectively in good agreement with the above bands which are characteristic of 2-substituted pyridines. Now, according to Rasmussen[10] the absorption band due to the bending frequencies of CH or the in-plane vibration of hydrogen in the aromatic ring appears in the vicinity of 1429 cm^{-1}. This band corresponds to the fourth, very strong band at 1428 cm^{-1} (II) and at 1430 cm^{-1} (III).

Aromatics have three highly characteristic absorption bands in the regions 1500~1600 cm^{-1} and these bands are assigned to the C=C stretching vibration of the three double bonds round the ring. Of these bands, Randall et al.[11] regarded a band in the regions 1575~1587 cm^{-1} as a positive indication of conjugation of a double bond with the aromatic ring. Brownlie[12] suggested that heterocyclic aromatics such as pyridine also give a similar pair of bands in the region from the C=C and the C=N links, although in this case the third skeletal vibration is usually at appreciably lower frequencies. According to Shindo[7], 2-substituted pyridines have three bands in the regions 1450~1600 cm^{-1} similar to those of substituted benzenes due to their ring double bond stretching vibrations. Compounds II and III show strong bands in this region. The bands at 1460(vvs), 1559(vvs) and 1574(m) cm^{-1} of compound II and 1460(vs), 1561 (vvs) and 1578 (s) cm^{-1} of compound III seem to arise from the 2-substituted pyridine rings, and especially the band at 1574 and 1578 cm^{-1} may be due to the pyridine ring conjugated with C=C double bond. Thus, it seems to be sure that both compounds II and III are 1,2-bis-(2-pyridyl)-ethylene.

7) H. Shindo, *Pharm. Bull.* (*Japan*), **5**, 472 (1957).
8) L. J. Bellamy, "The Infrared Spectra of Complex Molecules", Methuen & Co., London(1954), p. 69.
9) R. R. Randall et al., *Trans. Faraday Soc.*, **52**, 9 (1956).
10) R. S. Rasmussen, *Forthscr. Chem. org. Naturstoffe*, **5**, 131 (1948).
11) Randall et al., "The Infrared Determination of Organic Structures", von Nostrand, New York (1949).
12) Brownlie, *J. Chem. Soc.*, **1950**, 3062.

Generally, *trans*-disubstituted ethylenes show intense absorptions near 965 cm^{-1}. Rasmussen and Brattain[13] showed that these absorption bands appear only with *trans* double bond. These absorptions are attributed to the out-of-plane bending vibrations of =CH of the *trans*-disubstituted ethylenes and the absence of these bands can be regarded as conclusive evidence of the absence of *trans* double bond. The strong band at 968 cm^{-1} of II and the lack of this band in the spectrum of III lead to the conclusion that II is the *trans*-form and III is the *cis*-form.

The other sharp band at 1318 cm^{-1} in the spectrum of II is also lacking in the curve of III. According to Lunde et al.[6] *trans*-stilbene gives two weak absorptions at 1312 and 1342 cm^{-1} and these bands are lacking in *cis*-stilbene. Probably, these phenomena have some stereochemical significance which, however, can not be interpreted at the present time.

The melting point of III is lower by about seventy degrees than that of II, as shown in Table I. As the *cis*-isomer always melts at a very much lower temperature than the *trans*-isomer does[14], II and III seem to be a *trans*- and a *cis*-isomer, respectively. Their boiling points at 15 mmHg pressure are also shown in Table I. But it is impossible to distinguish between geometrical isomers from their boiling points, because no general rule as in the case of the melting points holds here.

The ultraviolet spectra of compounds II and III also support the above results as follows: The ultraviolet spectra of geometrical isomers such as those of stilbene[15,16], cinamic acid[16], phenylbutadiene[17] and azobenzene[18] have been investigated. They are composed of the E- (ethylenic) and the K- (conjugated) bands. The absorption intensities of the E-bands of the geometrical isomers are almost equal, while the K-band of the *cis*-form is about half as intense as that of the *trans*-form and lies at somewhat shorter wavelengths. It is well interpreted from the spatial arrangement of groups in these molecules. One of the isomers which approaches more closely to coplanarity exhibits a higher degree of resonance and shows more intense absorption at somewhat longer wavelengths[19]. The ultraviolet absorption curves of II and III are given in Fig. 2. Both have three strong to medium absorption bands in the region of the K-band (Table III). Compound II shows more intense absorption than the compound III and the absorption is located at the longer wavelengths. These curves are typical of geometrical isomers and compound II is a *trans*-isomer and compound III is a *cis*-isomer.

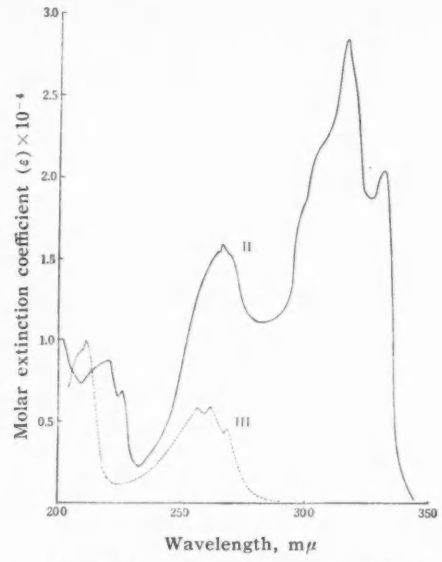


Fig. 2. Ultraviolet spectra of 1,2-bis-(2-pyridyl)-ethylene (II, *trans*; III, *cis*).

TABLE III. ULTRAVIOLET ABSORPTION BANDS OF 1,2-BIS-(2-PYRIDYL)-ETHYLENE

Compound II		Compound III	
$\lambda_{m\mu}$	ε	$\lambda_{m\mu}$	ε
220	8,770	211	9,920
226	6,830		
267	15,750	257	5,790
316	28,470	262	5,910
331	20,510	268	4,420
trans		*cis*	

λ, wavelength; ε, molar extinction coefficient.

The conclusion is that the 1,2-bis-(2-pyridyl)-ethylene described by Lénárt is a *trans*-isomer and the one separated by

13) R. S. Rasmussen and R. R. Brattain, *J. Chem. Phys.*, **15**, 131, 135 (1947).
14) M. Murakami, "Stereo-organic Chemistry (*Kozo-Yuki Kagaku*)", Asakura Publishers, Tokyo (1956), p. 181.
15) U. V. Solmssen, *J. Am. Chem. Soc.*, **65**, 2370 (1943).
16) A. E. Gillam et al., "An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry", Edward Arnold Publishers, London(1957), p. 269.
17) O. Grummitt et al., *J. Am. Chem. Soc.*, **73**, 3479 (1951).
18) R. N. Jones et al., *J. Chem. Soc.*, **1939**, 1315.
19) R. S. Mullikan, *J. Chem. Phys.*, **7**, 364 (1939).

the present author is a *cis*-isomer. The *cis*-isomer(III) is very hygroscopic while the other is not. It may be presumed that the *cis*-structure is very unstable and that it becomes stable by coupling with a water molecule.

The author wishes to thank Professor Sakujiro Kimura of Kyoto University for encouragement, to thank Professor Matsu'ura and his associates of Hiroshima University for recording infrared spectra, and also to thank Mr. Yamaguchi of this Laboratory for helpful assistance.

Chemical Laboratory
Kwansei Gakuin University
Nishinomiya

Synthesis of Aspartic and Glutamic Hydrazides and their Chromatographic and Ionophoretic Separation. C-Terminal Groups of Whale Insulin[1]

By Kozo NARITA and Yumiko OHTA

(Received February 11, 1959)

In the hydrazinolysis of peptides and proteins[2], non-C-terminal acidic amino acids or their amides residues in the polypeptide chain will be converted into α-mono- (derived from aspartyl and glutamyl residues) or di-hydrazides (derived from asparaginyl and glutaminyl residues). C-Terminal aspartic and glutamic acids or their amides will be found as free amino acids or as β- or γ-monohydrazides in the hydrazinolysates of proteins, respectively[3].

By quantitative determination of these hydrazides in the hydrazinolysates of proteins, the number of aspartyl, glutamyl, asparaginyl and glutaminyl residues in the original proteins could be estimated[3]. For that purpose, it is desirable to prepare standard substances for the identification and recovery determination by chromatography or ionophoresis.

Glutamic α- and γ-monohydrazides have previously been prepared[4,5], but the other hydrazides of the acidic amino acids have not heretofore been prepared, as far as we are aware. In the present paper, the synthesis of DL-aspartic α-hydrazide from phthaloyl-DL-aspartic α-methylester, of the isomeric β-hydrazide from L-asparagine, and of the dihydrazides of aspartic and glutamic acids from their diesters will be described. The present contribution also includes separation of these hydrazides by chromatography or ionophoresis, and its application to the hydrazinolysates of beef and whale insulins. The separation methods, however, were not satisfactory, since it was observed that appreciable amounts of some hydrazides were decomposed during the operation.

Experimental

Synthesis of DL-Aspartic α-Hydrazide.—A suspension of 14 g. of phthaloyl-DL-aspartic anhydride[6] in 120 ml. of absolute methanol was refluxed for 30 min. and a small amount of insoluble material was filtered off while it was warm. After being kept overnight, phthaloyl-DL-aspartic α-methyl ester crystallized as prisms. It was recrystallized from methanol; yield, 7.9 g., 43.8%, m.p. 181°C (reported[7] m.p. 182°C). The crude β-methyl ester obtained upon evaporation of the filtrate was recrystallized from water; yield, 3.9 g., 24.8%, m.p. 151~152°C (reported[7] m.p. 147~148°C).

A mixture of 4 g. of the α-ester, 50 ml. of methanol and 2.5 g. of 80% hydrazine hydrate was refluxed for 30 min. The precipitate of phthaloylhydrazine which resulted was filtered off and was washed with hot water. The combined solution of the filtrate and the washings

1) Some parts of this paper were presented at the 9th Annual Meeting of the Chemical Society of Japan, held at Kyoto in April, 1956.
2) S. Akabori, K. Ohno and K. Narita, This Bulletin, **25**, 214 (1952).
3) K. Ohno, *J. Biochem.*, **41**, 345 (1954).
4) S. Akabori and K. Narita, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **74**, 829 (1953).
5) K. Narita, ibid., **74**, 832 (1953).
6) F. E. King and D.A.A. Kidd, *J. Chem. Soc.*, **1951**, 2976.
7) F. E. King, J. W. Clark-Lewis and G. R. Smith, ibid., **1954**, 1046.

were adjusted to pH 3.5 with 1 N sulfuric acid. Enough amounts of Amberlite XE-58 (weak anion exchanger, free form) were added to the filtrate to remove sulfate ion, and the resin was filtered off after standing for 30 min. and was washed with water. The combined solution was concentrated in vacuo and two volumes of ethanol were added. An oily material solidified after being kept in a refrigerator and it was recrystallized from dilute ethanol; yield, 2.1 g., m.p. 143°C (with decomp.). It was found by paper chromatography and paper ionophoresis that this material was contaminated with a small amount of free aspartic acid. The aqueous solution of the crude material was again treated with Amberlite XE-58 in a similar manner as mentioned above. On evaporation of the filtrate to a small volume in vacuo, DL-aspartic α-hydrazide crystallized as needles. After addition of ethanol to the filtrate, a second crop of the hydrazide was obtained. The two crops combined were recrystallized from water-ethanol; yield, 1.1 g., 44%, m.p. 180°C (with decomp.).

Anal. Found: N, 27.7. Calcd. for $C_4H_9O_3N_3$: N, 28.6%.

Synthesis of L-Aspartic β-Hydrazide.—A mixture of 3 g. of L-asparagine, 2 ml. of ethanol and 2 g. of 80% hydrazine hydrate was refluxed for 30 min. and held overnight at room temperature. Ethanol was added to the syrup which was obtained on evaporation of the reaction mixture in vacuo and the β-hydrazide crystallized upon scratching of the wall of the vessel under ice cooling. The product was recrystallized from water-ethanol; yield, 2.8 g., 74.5%, m. p. 186°C. When the material was dried over phosphorous pentoxide at 100°C in vacuo, analysis indicated loss of 1.5 mol. water of hydration.

Anal. Found: N, 27.9. Calcd. for $C_4H_9O_3N_3$: N, 28.6%.

Synthesis of L-Aspartic and L-Glutamic Dihydrazides.—L-Aspartic and L-glutamic acids were converted into diethyl ester hydrochlorides, respectively, the free ester was extracted with ether as usual, and the solvent was removed after drying over sodium sulfate. Two and a half moles of hydrazine hydrate were added to the ethanolic solution of the ester, the mixture was held overnight at room temperature and the dihydrazide crystallized in needles. Recrystallization from aqueous ethanol gave about 60% yield in both cases. L-Aspartic α,β-dihydrazide, m.p. 164~165°C (with decomp.).

Anal. Found: N, 42.0. Calcd. for $C_4H_{11}O_2N_5$: N, 43.5%.

L-Glutamic α,γ-dihydrazide, m. p. 134~135°C (with decomp.).

Anal. Found: N, 39.2. Calcd. for $C_5H_{13}O_2N_5$: N, 40.0%.

Paper Chromatography.—Chromatography was performed by an ascending method using lutidine-water mixture (5 : 3, vol.) and Toyo No. 3 filter paper. In the case of multiple development the same solvent was repeatedly used. For the detection of both amino acid and hydrazide, 0.2% ninhydrin *n*-butanol solution (saturated with water) was used and for hydrazide only the ammoniacal silver nitrate solution was sprayed[8].

Paper Ionophoresis.—Toyo No. 3 filter paper (18×40 cm.) was generally used. For the separation of amino acids and hydrazides into three groups, namely, acidic, neutral and basic, neutral buffer of pH 6.4 was prepared in a similar manner as suggested by Lockhart and Abraham[9], except lutidine was used in place of collidine. For the mutual separation of neutral substances, 0.5 M acetic acid (pH 2.64) was used. Potential of 500 V. (12.5 V./cm.) was applied in each case. The current was 6 milliamp. in the case of neutral buffer and 2 milliamp. in dilute acetic acid. The ionophoretic rates of the hydrazides varied from experiment to experiment but the order of the rates did not change. Consequently, in the case of the measurements of relative rates of various hydrazides and the corresponding amides, those on the same paper sheet were compared.

Ion Exchange Chromatography.—Elution chromatography on a Dowex 50−X8 (200~400 mesh) column was tested to separate and estimate amino acid monohydrazides according to the procedure of Moore and Stein[10]. C-Terminal amino acids with the exception of terminal basic amino acids must be present as neutral or acidic substances in the hydrazinolysate of proteins. Since basic materials were adsorbed on the top of the resin column which equilibrated with 0.1 or 0.2 M citrate buffer of pH 3.4, neutral substances were eluted with citrate buffers of several pH's from a short column (0.9×15 cm. or 0.9×30 cm.). In the present experiments, the behaviors of alanine, aspartic β- and glutamic α-hydrazides were mainly studied with regard to the study on insulin.

Hydrazinolysis of Insulin and Treatment of the Product.—Beef and whale insulins studied were kindly supplied by Dr. J. Lens, Organon, Oss, and Shimizu Pharmaceutical Co., respectively. Anhydrous hydrazine was prepared in a similar manner as suggested by Ohno[3]. About 30 mg. of insulin was dissolved in 0.5 ml. of anhydrous hydrazine and heated at 100°C for 8 hr. The hydrazinolysate was taken into dryness over calcium chloride in vacuo at room temperature. In paper ionophoresis, the dried residue was dissolved in a minimum volume of water, an aliquot was applied to Toyo No. 50 paper, thick paper (18×40 cm.), along the starting line, and a potential gradient of 500 V. was applied at pH 6.4 in lutidine-acetic acid buffer. After ionophoresis and air drying, strips from both sides of the paper sheet were cut off and treated with the silver nitrate reagent to detect hydrazides. Using these as a guide, the remainder of the sheet containing neutral substances was cut and they were eluted with water by the technique of Sanger and Tuppy[11]. The wetting top of the cut

8) A mixture of one part of 0.1 N $AgNO_3$ and one part of 0.5 N NH_4OH solution.

9) I. M. Lockhart and E. P. Abraham, *Biochem. J.*, **58**, 633 (1954).

10) S. Moore and W. H. Stein, *J. Biol. Chem.*, **192**, 663 (1951).

11) F. Sanger and H. Tuppy, *Biochem. J.*, **49**, 463 (1951).

paper strip was applied to another paper sheet (Toyo No. 3) and subjected to ionophoresis at pH 2.64 or one- or two-dimensional chromatography.

For the characterization of C-terminal amino acid with the exception of the basic one, asparagine and glutamine, the following technique is also applicable. After ionophoresis of the hydrazinolysate at pH 6.4, the area of hydrazides which traveled to cathode was cut off and the remaining area which contained C-terminal amino acid and monohydrazides of acidic amino acids was then developed with phenol and lutidine two-dimensionally. In this case, it is preferable to develop them first with phenol and then lutidine. During the first development, most of the monohydrazides were destroyed and several very faint unidentified spots could be observed near the phenol front. This procedure might be useful to characterize the C-terminal group of polypeptide of a small molecule, and was successfully used for several cytochromes[12] and for insulin shown in Fig. 1.

In the quantitative determination of the C-terminal groups of insulin, the dried hydrazinolysate was dissolved in 0.5 ml. of 0.05~0.1 N hydrochloric acid 0.5 ml. of 0.2 M citrate buffer (pH 3.5) was added and any insoluble material was centrifuged off, if necessary. A half milliliter of the supernatant was applied to the Dowex 50 column (0.9×15 cm.) equilibrated with 0.2 M citrate of pH 4.23 and elution was started.

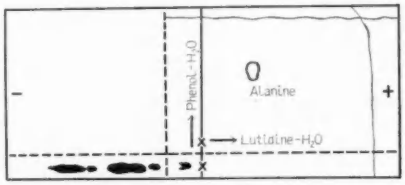


Fig. 1. Ionophoresis at pH 6.40 and subsequent chromatography of the hydrazinolysate of whale insulin. Mark X and broken line indicate original spot and line to be cut before chromatography, respectively. Black and white spots indicate ammoniacal silver nitrate and ninhydrin positive, respectively.

Results and Discussion

Paper Chromatography. — Multiple development technique was used in lutidine-water, since the difference between *Rf* values of the hydrazides was slight in a single development. However, no remarkable effect in resolution of the spots resulted by repeating the development with the same solvent more than twice. *Rf* values of the hydrzaides of acidic amino acids were recorded in Table I.

TABLE I. *Rf* VALUES OF ASPARTIC AND GLUTAMIC HYDRAZIDES*

Number of development	1	2	3
Aspartic α-hydrazide	0.23	0.41	0.48
Aspartic β-hydrazide	0.15	0.33	0.39
Aspartic α,β-dihydrazide	—	0.36	—
Glutamic α-hydrazide	0.24	0.43	0.50
Glutamic γ-hydrazide	0.18	0.37	0.45
Glutamic α,γ-dihydrazide	—	0.44	—

* Lutidine-water (5 : 3, vol.) and the ammoniacal silver nitrate solution were used as the solvent and the reagent, respectively.

Paper Ionophoresis.—Acidic, neutral and basic substances were separated during ionophoresis at pH 6.4, but the acidic amino acid monohydrazides and neutral amino acids could not be separated from each other in this medium. Mutual separation of neutral amino acids has usually been performed in either an acidic or alkaline medium based on the difference of the dissociation constants of their carboxyl or amino group. In the present experiments, acidic pH was used, since amino acid hydrazide seemed to be labile in alkaline medium. The ionophoretic rates of aspartic and glutamic hydrazides to cathode on a paper at pH 2.64 were in the following order:

Glutamic α,γ-dihydrazide>
Aspartic α,β-dihydrazide>
Glutamic α-hydrazide>
Aspartic α-hydrazide>
Glutamic γ-hydrazide>
Aspartic β-hydrazide

The pK'_{COOH} values of aspartic and glutamic monohydrazides are unknown but those of the corresponding amides have been reported[13]. Therefore, the distance that the monohydrazides traveled to cathode during ionophoresis on the

TABLE II. DISTANCES TRAVELED TO CATHODE DURING IONOPHORESIS OF ASPARTIC AND GLUTAMIC HYDRAZIDES AND THE CORRESPONDING AMIDES AT pH 2.64*

	Hydrazid	Amide	
	Distance	Distance	pK'_{COOH}[13]
Aspartic β-	6.1 cm.	4.4 cm.	2.02
Glutamic γ-	6.7	4.8	2.17
Aspartic α-	7.5	—	2.97
Glutamic α-	8.8	8.3	3.81

* Toyo No. 3 filter paper (18×40 cm.), 0.5 M acetic acid, 500 V., 2 milliamp. and 120 min. were used.

12) K. Titani and H. Ishikura, *J. Biochem.*, **44**, 499 (1957).

13) D. M. Greenberg, "Amino Acids and Proteins", Charles C. Thomas Publishers, Springfield (1951), p. 430.

same paper sheet in acidic medium were compared with those of the corresponding amides, to find relationship between the dissociation constant and behavior on the paper (Table II).

The parallel relationship between the ionophoretic rate and the dissociation constant of the amides was observed. Comparing the rates of the amides with those of the corresponding hydrazides, it is apparent that the dissociation constant of the latter is slightly higher than that of the former, and that the difference between the dissociation constant of the hydrazide of α-position and that of ω-position is smaller than that of the corresponding amides. In the ionophoresis performed under the conditions used, the hydrazides in the following pairs were barely separated from one another: Aspartic α-hydrazide and glutamic γ-hydrazide, and glutamic γ-hydrazide and aspartic β-hydrazide. Futhermore, it was observed that the dihydrazides were partially decomposed into both the isomers of the monohydrazides liberating hydrazine in acidic medium.

Ion Exchange Chromatography.—In the ion exchange chromatography, no hydrazides eluted with 0.1 M citrate of pH 3.45 from the 30 cm. column, although aspartic and glutamic acids and alanine eluted each forming a single sharp peak, respectively. When the pH of the buffer was changed to 4.34, leucine, aspartic β- and glutamic γ-hydrazides successively came out from the column. The recoveries of the hydrazides in effluent were only a small percentage using the ninhydrin color yields of the Table III, in which the ratio of ninhydrin color value per mol. hydrazide to that of leucine is listed[10].

TABLE III. NINHYDRIN COLOR YIELDS OF ACIDIC AMINO ACID HYDRAZIDES

Hydrazide	Color yield
Leucine	1.00
Aspartic α-hydrazide	0.93
Aspartic β-hydrazide	1.05
Aspartic α, β-dihydrazide	0.79
Glutamic α-hydrazide	0.85
Glutamic γ-hydrazide	0.69
Glutamic α, γ-dihydrazide	0.48

It was observed that the recoveries of the hydrazides became lower the more acidic the resin surface and the longer the time of contact with the resin. In order to elute hydrazides more rapidly, the length of the column was halved and the ionic strength of the buffer was doubled. Concerning insulin, alanine, aspartic β- and gultamic α-hydrazides could be separated from one another, but aspartic β- and glutamic γ-hydrazides and leucine overlapped in such a column system. Recoveries of the hydrazides were still low under such conditions and further unknown degradation products of the hydrazides eluted gradually and the base line between the peaks of aspartic β- and glutamic α-hydrazides was relatively high. In the quantitative estimation, the base line behind the peak of glutamic α-hydrazide was used.

C-Terminal Groups of Whale and Beef Insulins.—Characterizations of C-terminal amino acids and free carboxyl groups of whale insulin were carried out by means of hydrazinolysis-ionophoresis method described in the experimental section. Alanine, aspartic β- and glutamic α-hydrazides could be identified. These results indicate that the C-terminal groups of the hormone must be alanine and asparagine and that all of the non-C-terminal carboxyl groups belong to glutamic acid residues.

Quantitative estimation of these groups was done by chromatography on a Dowex 50 column. For this purpose it is necessary to determine to what extent known amounts of amino acids could be recovered after treatment with hydrazine and chromatography. A mixture of alanine, asparagine and isoglutamine was heated with anhydrous hydrazine for 8 hr. at 100°C and the reaction mixture was treated according to the procedures described in the experimental section. The recoveries for those are recorded in Table IV. A typical elution curve of the hydrazinolysate of whale insulin is shown in Fig. 2

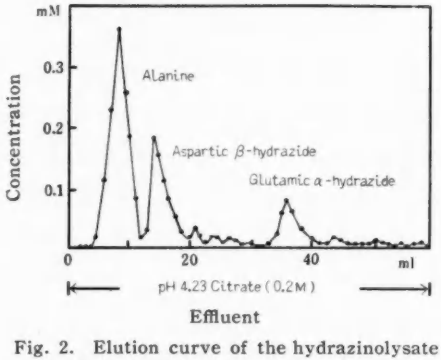


Fig. 2. Elution curve of the hydrazinolysate of whale insulin from Dowex 50 column (0.9×15 cm.).

TABLE IV. RECOVERIES OF AMINO ACIDS AFTER HYDRAZINOLYSIS AND CHROMATOGRAPHY

Material	Product after hydrazinolysis	Recovery after hydrazinolysis and chromatography	Recovery after chromatography	Recovery calculated for hydrazinolysis
Alanine	Alanine	0.48	1.0	0.48
Asparagine	Aspartic β-hydrazide	0.25	0.39	0.64
Isoglutamine	Glutamic α-hydrazide	0.088	0.31	0.29

TABLE V. C-TERMINAL GROUPS AND GLUTAMYL RESIDUES IN WHALE AND BEEF INSULINS*

Insulin		Observed value: Average	Observed value: Range	Corrected value
Whale**	Alanine	0.54	0.41~0.65	1.1
	Aspartic β-hydrazide	0.26	0.22~0.29	1.0
	Glutamic α-hydrazide	0.25	0.20~0.29	2.8
Beef***	Alanine	0.46		1.0
	Aspartic β-hydrazide	0.28		1.1
	Glutamic α-hydrazide	0.14		1.6

* Figures are expressed as mol. per mol. insulin of which molecular weight is assumed to be 6,000.

** Average value for four experiments.

*** Value for single experiment.

and the analytical data of whale and beef insulins are summarized in Table V.

It appears probable that the C-terminal groups of both the insulins (assumed molecular weight, 6,000) are each one mole alanine and asparagine which are consistent with the results of Sanger et al.[14], Harris et at.[15,16] and Chibnall et al.[17] but differ from our previous results[2], in which we reported an additional C-terminal glycine but missed asparagine which escaped from the detection in the earlier method. The main reason which caused such a difference may be attributed to the drastic conditions used in the previous experiments and non-C-terminal glycine might be erroneously identified.

To confirm the singleness of the peak of alanine in Fig. 2, an aliquot of the hydrazinolysate of whale insulin was chromatographed on a Dowex 50 column (0.9×15 cm.) which equilibrated with 0.1 M citrate of pH 3.46. As is shown in Fig. 3, a small peak appeared before alanine and it corresponded to aspartic acid which might be derived from the hydrazide during chromatography. The amount of alanine found in this system was 0.8 mol. per mol. insulin.

In connection with the number of free

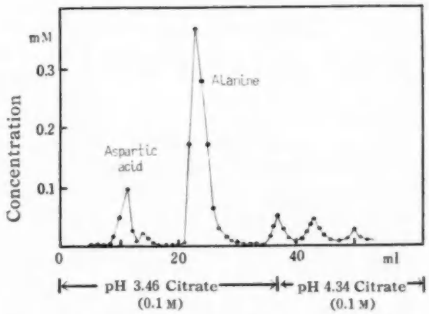
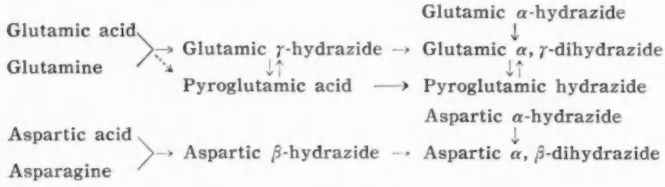


Fig. 3. Chromatogram of the hydrazinolsate of whale insulin on Dowex 50 column (0.9×15 cm.). Concentration and pH of the buffer differ with those in Fig. 2.

carboxyl groups, the present results appear to be of little value, since significant differences were obsereved between the values derived by reduction method and by hydrazinolysis have been obtained with lysozyne[3,18] and the protein of tobacco mosaic virus[19]. As is well known, recoveries of some amino acids, especially aspartic and glutamic acids, after hydrazine treatment are pretty low[20,21]. It was found that one of the main decomposition products was the corresponding hydrazide,

14) F. Sanger, E. O. P. Thompson and R. Kitai, *Biochem. J.*, **59**, 509 (1955).
15) J. I. Harris and C. H. Li, *J. Am. Chem. Soc.*, **74**, 2944 (1952).
16) J. I. Harris, F. Sanger and M. A. Naughton, *Arch. Biochem. Biophys.*, **65**, 427 (1956).
17) A. C. Chibnall and M. W. Rees, *Biochem. J.*, **68**, 105 (1958).
18) A. C. Chibnall, C. H. Haselbach, J. L. Mangan and M. W. Rees, ibid., **68**, 122 (1958).
19) L. K. Ramachandran and K. Narita, *Biochim. et Biophys. Acta*, **30**, 616 (1958).
20) R. H. Locker, ibid., **14**, 533 (1954).
21) C.-I. Niu and H. Fraenkel-Conrat, *J. Am. Chem. Soc.*, **77**, 5882 (1955).

which was identified by paper chromatography. The situation of aspartic and glutamic acids is quite complicated. When glutamic acid alone, for example, was heated with hydrazine and the reaction products were analyzed by chromatography, glutamic acid, glutamic γ-hydrazide, glutamic α, γ-dihydrazide, pyroglutamic acid, pyroglutamic hydrazide and an unknown product were identified. The reaction products of glutamine, glutamic α- and glutamic γ-hydrazides, aspartic acid, asparagine, aspartic α- and aspartic β-hydrazides with hydrazine were analyzed, respectively. Summarizing these results which were obtained, the following reaction scheme could be deduced.



Since free acidic amino acid has never been detected in the reaction mixture of hydrazine with the amide of acidic amino acid, C-terminal asparagine and glutamine can be estimated by hydrazinolysis method by the use of appropriated recovery factors. However, it appears difficult to determine the numbers of non-C-terminal acidic amino acids or their amides residues by hydrazinolysis, owing to the fact that both of them produce the same product, dihydrazide.

In the quantitative determination of C-terminal asparagine or glutamine, elution chromatography described in the present paper seems not to be suitable, since hydrazide derived from the terminal group is decomposed in significant quantity during operation. The dinitrophenyl derivatives of aspartic β- and glutamic γ-hydrazides from the hydrazinolysate of protein by the method III of Akabori et al.[22] or slightly modified method[19], can be separated from one another on two-dimensional paper chromatogram[23,24] developed with Levy's solvent system[25] and this method appears to be more suitable than the present one.

Summary

Aspartic α- and β-monohydrazides and aspartic α, β- and glutamic α, γ-dihydrazides were prepared and their qualitative separation has been performed by means of paper ionophoresis and chromatography. During ionophoresis in acidic medium, the dihydrazide partially decomposed into the isomers of monohydrazides liberating hydrazine. The hydrazinolysis products of whale and beef insulins were analyzed by the aid of elution chromatography on a Dowex 50 column and it was observed that the C-terminal positions were occupied by each one mole of alanine and asparagine in both cases. Furthermore, the present experiments suggested that all of the non-terminal carboxyl groups of the hormone belonged to only glutamic acid residues. Complicated reaction of the acidic amino acids or their amides with hydrazine was discussed.

The present authors are grateful to Professor S. Akabori for his interest and encouragement in these studies, to Shimizu Pharmaceutical Co. and Dr. J. Lens for generous supply of whale and beef insulins, respectively.

Institute for Protein Research
Osaka University
Nakanoshima, Osaka (K.N.)

Department of Chemistry
Ochanomizu Women's University
Bunkyo-ku, Tokyo (Y.O.)

Reprint request should be quoted to K. Narita.

22) S. Akabori, K. Ohno, T. Ikenaka, Y. Okada, H. Hanafusa, I. Haruna, A. Tsugita, K. Sugae and T. Matsushima, This Bulletin, **29**, 507 (1956).
23) K. Narita, unpublished experiments.
24) Y. Kawanishi, K. Iwai and T. Ando, Symposium on Protein Structure, held at Osaka in November, 1958.
25) A. L. Levy, "Methods of Biochemical Analysis", Vol. II, Interscience Publishers, New York (1955), p. 397.

*Thermodynamic Studies on Cobalt Complexes. IV. On the Thermal Dissociation and the Solubility of Aquopentamminecobalt(III) Chloride**

By Motoshichi MORI, Ryokichi TSUCHIYA and Yasuhiro OKANO

(Received February 14, 1959)

In the preceding papers the authors determined the standard free energy of formation of hexamminecobalt(III) chloride in the solid state by measuring its solubility in water[1] and employing the known value of the standard free energy of formation of hexamminecobalt(III) ion. The standard free energy of formation of chloropentamminecobalt(III) chloride in the solid state was also determined by measuring the dissociation pressure of hexamminecobalt(III) chloride[2]. In the present report which is a part of the thermodynamic studies on coordination compounds, the standard free energy of formation of aquopentamminecobalt(III) chloride was determined by measuring its dissociation pressure, and its activity coefficient in the saturated aqueous solution by measuring its solubility. On the basis of these experimental results discussions were conducted on the thermodynamic stability of hexamminecobalt(III), aquopentamminecobalt(III) and chloropentamminecobalt(III) chlorides in the solid state and in the aqueous solution.

Experimental

Aquopentamminecobalt(III) chloride was prepared by the method of Jörgensen[3]. The measurement of its dissociation pressure and rate of thermal dissociation was carried out with the same apparatus described in the preceding paper[2].

The solubility of this complex was determined by analyzing the cobalt content of its saturated aqueous solution by iodometry.

Results and Discussion

Dissociation Pressure of Aquopentamminecobalt(III) Chloride.—As we confirmed by the spectrophotometric measurements the fact that the products of thermal dissociation of aquopentamminecobalt(III) chloride were chloropentamminecobalt(III) chloride and water vapour, the dissociation pressure observed is the vapour tension of water formed by the following reaction;

$$[Co(NH_3)_5OH_2]Cl_3(s) = [Co(NH_3)_5Cl]Cl_2(s) + H_2O(g)$$

The results of measurement of the dissociation pressure are given in Table I. The logarithms of the dissociation

TABLE I. DISSOCIATION PRESSURE OF AQUOPENTAMMINECOBALT(III) CHLORIDE

Temp. °C	$1/T\times10^3$	Dissociation pressure mmHg	$\log p_{mm}$
21	3.400	1.65	0.2175
25	3.356	2.15	0.3324
28	3.310	2.50	0.3979
31	3.288	3.04	0.4829
32	3.278	3.09	0.4900
34	3.256	3.44	0.5366
35	3.246	3.59	0.5551
38	3.214	4.20	0.6233
40	3.195	4.74	0.6758
43	3.164	5.44	0.7356
45	3.144	5.99	0.7774
48	3.114	6.93	0.8407

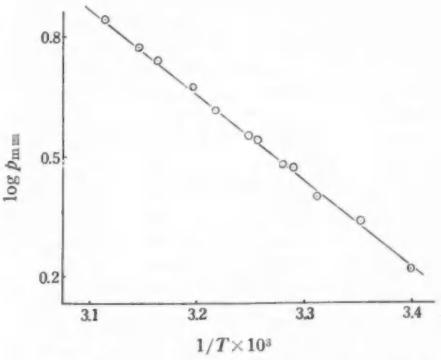


Fig. 1. Relationship between the dissociation pressure of aquopentamminecobalt(III) chloride and the temperature.

* Read at the Symposium on Coordination Compounds of the Chemical Society of Japan held in Nov., 1958.

1) M. Mori, R. Tsuchiya and Y. Okano, This Bulletin, **32**, 462 (1959).

2) M. Mori and R. Tsuchiya, ibid., **32**, 467 (1959).

3) S. M. Jörgensen, *Z. anorg. u. allgem. Chem.*, **17**, 461 (1898).

pressure p_{mm} are plotted against the reciprocal of the absolute temperature in Fig. 1, and an almost straight line is obtained. The equation of the straight line calculated by the method of least squares is

$$\log p_{mm} = 7.5888 - 2166.0/T$$

This equation gives the heat of dissociation ΔH as 9908 cal., and the free energy change of dissociation ΔG° as

$$\Delta G^\circ = -RT \ln p_{atm} = 9908 - 21.54T \quad (1)$$

The value of the free energy change of dissociation at 25°C is $\Delta G^\circ_{298} = 3488$ cal. and that of the entropy change is $\Delta S^\circ_{298} = 21.54$ e. u.

In the preceding paper[2] the standard free energy of formation of chloropentamminecobalt(III) chloride was determined by measuring the dissociation pressure of hexamminecobalt(III) chloride as

$$\Delta G^\circ = -254008 + 365.99T \quad (2)$$

By using the standard free energy of formation of $H_2O(g)$ at 25°C, $\Delta G^\circ_{298} = -54636$ cal.[4] and its heat of formation, $\Delta H_{298} = -57798$ cal.[4], the standard free energy of formation of H_2O as a function of temperature is given by

$$\Delta G^\circ = -57798 + 10.607T \quad (3)$$

Combining Eq. 3 with Eqs. 2 and 1, we get the following equation for the standard free energy of formation of aquopentamminecobalt(III) chloride in the solid state,

$$\Delta G^\circ = -321714 + 398.13T \quad (4)$$

The value of ΔG° at 25°C is $\Delta G^\circ_{298} = -203.024$ kcal.

The Rate of Thermal Dissociation of Aquopentamminecobalt(III) Chloride.—The results of the measurement of the rate of thermal dissociation of aquopentamminecobalt(III) chloride are shown in Table II and Fig. 2.

The velocity constant k at the time when the dissociation begins, is assumed to be given by the tangent of the curve at the origin in Fig. 2. When $\log k$ is plotted against the reciprocal of the absolute temperature, $1/T$, an approximately straight line is obtained as shown

TABLE II. RATE OF DISSOCIATION OF AQUOPENTAMMINECOBALT(III) CHLORIDE

Temp., °C	33	38	43
Time, min.	Dissociation pressure, mmHg		
1	—	—	0.60
2	—	0.55	0.90
3	0.55	0.75	1.10
5	0.70	1.00	1.25
7	—	—	1.40
10	0.90	1.25	1.60
15	1.00	1.35	1.85
20	1.10	1.45	2.10
25	—	1.55	2.35
30	1.15	1.60	2.55
35	—	—	2.70
40	1.20	1.70	2.90
50	—	1.80	3.15
1 hr.	1.25	1.90	3.59
1.5	1.35	2.10	4.33
2	1.45	2.40	—
2.5	1.55	2.70	—
3	1.65	3.05	—
4	1.85	3.45	—
$1/T\times10^3$	3.267	3.214	3.164
k	0.206	0.352	0.628
$\log k$	$\bar{1}.3139$	$\bar{1}.5465$	$\bar{1}.7980$

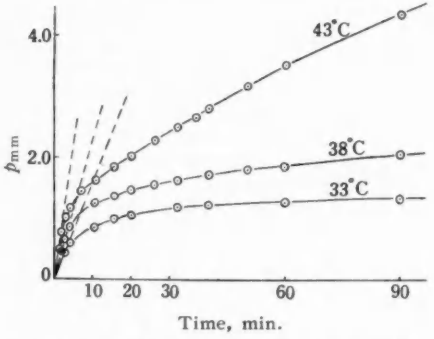


Fig. 2. Rate of dissociation of aquopentamminecobalt(III) chloride.

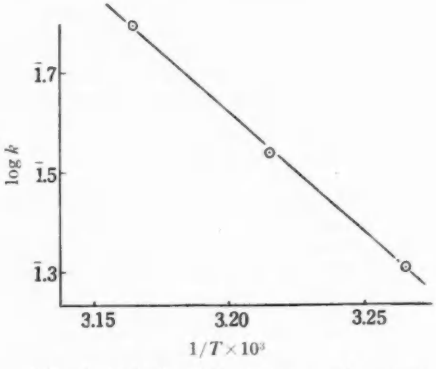


Fig. 3. Relationship between the rate constant and the reciprocal of the absolute temperature.

4) F. D. Rossini et al., "Selected Values of Chemical Thermodynamic Properties", United States Government Printing Office, Washington (1952), p. 9.

in Fig. 3, which gives 21.47 kcal. as the activation energy of the dissociation of aquopentamminecobalt(III) chloride.

Solubility and Activity Coefficient of Aquopentamminecobalt(III) Chloride. — Since the activity coefficient of aquopentamminecobalt(III) chloride has never been found in any literature, the value in the saturated aqueous solution was calculated from the solubility data determined in the present study.

First, by using the standard free energy of formation of aquopentamminecobalt-(III) ion in unit activity at 25°C, $\Delta G^\circ_{298} = -104.5$ kcal.[5] and its heat of formation, $\Delta H_{298} = -192.9$ kcal.[6], the standard free energy of formation is obtained as a function of temperature:

$$\Delta G^\circ = -192900 + 296.55T \quad (5)$$

Combining Eq. 5 with Eq. 6 for the standard free energy of formation of chloride ion,

$$\Delta G^\circ = -40023 + 29.1T \quad (6)$$

[2]

and that of aquopentamminecobalt(III) chloride in the solid state, Eq. 4 obtained above, the free energy change of the solution of aquopentamminecobalt(III) chloride is given by

$$\Delta G^\circ = 8745 - 14.28T \quad (7)$$

The value, 8745 cal. is obtained as the heat of the solution of this complex and $\Delta S^\circ_{298} = 14.28$ e. u. is obtained as the entropy change at 25°C.

On the other hand, the equilibrium constant, K, of the solution of aquopentamminecobalt(III) chloride represented by

$$[Co(NH_3)_5OH_2]Cl_3(s) \rightleftarrows [Co(NH_3)_5OH_2]^{3+}\ (aq.) + 3Cl^-\ (aq.)$$

is given by

$$K = \exp(-\Delta G^\circ/RT) \quad (8)$$

If the molality of the solute is expressed by m, the mean activity coefficient, $\gamma_\pm$, in a 1—3 valency type salt[1] is given by

$$\gamma_\pm = \sqrt[4]{K/27}/m \quad (9)$$

Further, if the solubility of aquopentamminecobalt(III) chloride determined by iodometry is expressed by C (mol./l.) and specific gravity of the saturated aqueous solution measured by the hydrometer, d, the molality m is given by

$$m = 1000C/(1000d - MC) \quad (10)$$

where M is the molecular weight of this complex. Thus, the mean activity coefficient $\gamma_\pm$ can be calculated by combining Eqs. 7—10.

The values of the solubility of aquopentamminecobalt(III) chloride and the values of the mean activity coefficient are listed in Table III.

The activity coefficient of aquopentamminecobalt(III) chloride in such concentrated aqueous solutions has never been reported in the past.

Relationship between the Solubility and the Free Energy Change of Solution of Hexamminecobalt(III) and Aquopentamminecobalt(III) Complexes. — From Eqs. 8 and 9, the following equation is derived:

$$\Delta G^\circ = -2.303RT\ (\log 27 + 4\log m + 4\log \gamma_\pm) \quad (11)$$

In the range where $\log \gamma_\pm$ is a linear function of $\log m$ at 25°C, Eq. 11 can be rearranged as

$$\Delta G^\circ_{298} = \alpha + \beta \log m \quad (12)$$

where α and β are constants. Furthermore, if m is approximately proportional to the molar concentration C, Eq. 12 becomes

$$\Delta G^\circ_{298} = \alpha' + \beta' \log C \quad (13)$$

where α' an β' are constants.

When the data of the free energy change, ΔG°_{298}, of the solution of hexamminecobalt-(III) chloride, bromide, nitrate and perchlorate reported in the preceding paper[1] as well as that of aquopentamminecobalt-(III) chloride listed in Table III are plotted

TABLE III. SOLUBILITY OF AQUOPENTAMMINECOBALT(III) CHLORIDE AND THE RESULTS OF CALCULATION

Temp. °C	Solubility C	Molality m	Free energy change of solution, ΔG°	Equilibrium constant of solution, K	$\gamma\pm$
15	0.7317	0.8262	4631	3.061×10^4	0.07023
20	0.7661	0.8639	4559	3.976×10^4	0.07171
25	0.8051	0.9106	4488	5.111×10^4	0.07244
30	0.8388	0.9516	4417	6.518×10^4	0.07366

5) A. B. Lamb and A. T. Larson, *J. Am. Chem. Soc.*, **42**, 2038 (1920).

6) F. D. Rossini et al., "Selected Values of Chemical Thermodynamic Properties", United States Government Printing Office, Washington (1952), p. 255.

TABLE IV. THERMODYNAMIC FUNCTIONS IN THE THERMAL DISSOCIATION AND SOLUTION OF HEXAMMINECOBALT(III) AND AQUOPENTAMMINECOBALT(III) CHLORIDES

Reaction	ΔG°_{298}	ΔH_{298}	ΔS°_{298}
$[Co(NH_3)_5NH_3]Cl_3(s) \rightarrow [Co(NH_3)_5Cl]Cl_2(s)+NH_3(g,\ 1\ atm.)$	5672	9612	13.22
$[Co(NH_3)_5OH_2]Cl_3(s) \rightarrow [Co(NH_3)_5Cl]Cl_2(s)+H_2O(g,\ 1\ atm.)$	3488	9908	21.54
$[Co(NH_3)_5NH_3]Cl_3(s) \rightarrow [Co(NH_3)_5NH_3]^{3+}(aq.\ a=1)+3Cl^-(aq.\ a=1)$	6003	8567	8.61
$[Co(NH_3)_5OH_2]Cl_3(s) \rightarrow [Co(NH_3)_5OH_2]^{3+}(aq.\ a=1)+3Cl^-(aq.\ a=1)$	4488	8745	14.28

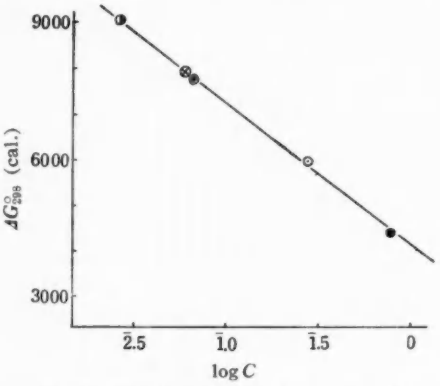


Fig. 4. Relationship between the free energy change of solution and the solubility.
⊙, $[Co(NH_3)_6]Cl_3$
◉, $[Co(NH_3)_6]Br_3$
⊗, $[Co(NH_3)_6](NO_3)_3$
◑, $[Co(NH_3)_6](ClO_4)_3$
●, $[Co(NH_3)_5OH_2]Cl_3$

against the logarithm of their molar concentration C, they all fall on a straight line as shown in Fig. 4. This means that Eq. 13 is applicable to 1—3 valency type complexes described above. Therefore, the free energy change of a solution of a complex of 1—3 valency type can be calculated by using Fig. 4, provided its solubility C is known.

Thermodynamic Stability of Hexamminecobalt(III), Aquopentamminecobalt(III) and Chloropentamminecobalt(III) Chlorides.—The thermodynamic functions in the thermal dissociation and solution of hexamminecobalt(III) and aquopentamminecobalt(III) chlorides at 25°C are summarized in Table IV.

Although the heat of dissociation of hexamminecobalt(III) chloride is close to that of aquopentamminecobalt(III) chloride as shown in Table IV, the entropy change of dissociation of the former is remarkably smaller than that of the latter. Therefore, it is inferred that the difference between the free energy changes of dissociation of the two complexes is due to the difference between the entropy changes. The heat of solution of hexamminecobalt(II) chloride is again close to that of aquopentamminecobalt(III) chloride, and the difference between the free energy changes of solution of these two complexes must be due to the difference between their entropy changes. In other words, it is concluded that the entropy effect plays an important role in those reactions listed in Table IV.

From the solubility data[7] and the activity coefficient[8] of chloropentamminecobalt(III) chloride, its free energy change of solution is calculated as $\Delta G^\circ_{298}=6865$ cal. By using this value and the free energy changes of thermal dissociation and solution of hexamminecobalt(III) and aquopentamminecobalt(III) chlorides, the standard free energy levels of hexamminecobalt(III), aquopentamminecobalt(III) and chloropentamminecobalt(III) chlorides in the solid state and in the aqueous solution in unit activity are computed and shown in Fig. 5. This figure clearly shows the degree of thermodynamic stability of these complexes. The order of the thermodynamic stability is found to coincide with the spectrochemical series[9,10].

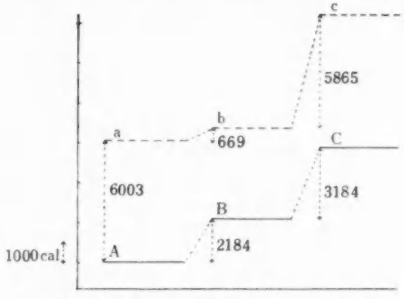


Fig. 5. Standard free energy levels.
A, $[Co(NH_3)_6]Cl_3(s)$
B, $[Co(NH_3)_5OH_2]Cl_3(s)$
C, $[Co(NH_3)Cl]Cl_2(s)$
a, $[Co(NH_3)_6]^{3+}(aq.)+3Cl^-(aq.)$
b, $[Co(NH_3)_5OH_2]^{3+}(aq.)+3Cl^-(aq.)$
c, $[Co(NH_3)_5Cl]^{3+}(aq.)+2Cl^-(aq.)$

7) J. N. Brönsted and A. Petersen, *J. Am. Chem. Soc.*, **43**, 2265 (1921).
8) B. Adell, *Z. anorg. u. allgem. Chem.*, **246**, 303 (1941).
9) R. Tsuchida, This Bulletin, **13**, 388, 436 (1938).
10) Y. Shimura and R. Tsuchida, ibid., **29**, 311 (1956).

Summary

1. The standard free energy of formation of aquopentamminecobalt(III) chloride in the solid state was calculated by measuring its dissociation pressure.

2. From this value and the standard free energy of formation of aquopentamminecobalt(III) ion, the free energy change of the solution of aquopentamminecobalt(III) chloride was calculated. From this value and the solubility data the activity coefficient of aquopentamminecobalt(III) chloride in the saturated aqueous solution was calculated.

The free energy changes of the solutions of hexamminecobalt(III) chloride, bromide, nitrate and perchlorate as well as of aquopentamminecobalt(III) chloride were found to be a linear function of the logarithms of their solubilities.

3. The thermodynamic stability of hexamminecobalt(III), aquopentamminecobalt(III) and chloropentamminecobalt(III) chlorides in the solid state and in the aqueous solution was discussed.

Department of Chemistry
Faculty of Science
Kanazawa University
Kanazawa

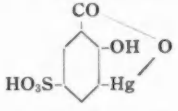
Rheological Properties of Gels. Viscoelasticity of Mercury Sulfosalicylate Solution

By Takaaki DANNO

(Received February 18, 1959)

The study on the visco-elastic properties of agar-agar gel was reported previously[1]. The agar gel shows interesting flow properties superposed on the elastic ones, especially in its softening and melting region. These are interesting from the view point of the relation between the rheological properties and the change of internal structure in the course of the melting of gel. More detailed experiments, however, could not be carried out by reason of the structural limit of our instruments.

On the other hand, mercury sulfosalicylate solution has interesting elasto-viscous properties, as shown by T. Nakagawa[2] who attributed the "Spinnbarkeit" of the solution to its elastic property. The solution is very elastic and also has viscous flow properties. It has been assumed[3] that the structural formula of mercury sulfosalicylate is



It is interesting to seek the origin of strong elasticity of the solution of such a simple substance.

The author measured the visco-elastic parameters of them and studied their dependence on frequency, amplitude, concentration, temperature change, and other factors, by using the coaxial dynamical rheometer.

Experimental

As the experimental procedure for studying the visco-elastic properties of mercury sulfosalicylate solution, the author adopted the method of coaxial type rheometer, which was designed by T. Nakagawa[4].

In this dynamic method for measuring visco-elastic constants, a sinusoidal oscillation is applied at the top of a torsion wire, from which the inner cylinder is suspended, and whose torsion constant is k dyn./cm. Then, the displacement of the top of the torsion wire is given by

$$\theta = \theta_0 \sin \omega t \tag{1}$$

and the equation of motion of the inner cylinder is

$$I\ddot{\theta} + R\dot{\theta} + E\theta = k(\theta - \theta) \tag{2}$$

1) T. Danno, *Bull. Tokyo Gakugei Univ.*, **6**, 103 (1955).
2) T. Nakagawa, This Bulletin, **25**, 93 (1952).
3) Wo. Ostwald and M. Mertens, *Kolloid-Beih.*, **23**, 242 (1926).
4) T. Nakagawa and M. Seno, This Bulletin, **29**, 471 (1956).

where I is the moment of inertia of the inner cylinder, and R and E are the viscous and elastic resistance respectively of the solution between the two cylinders. The stationary solution of this equation is

$$\left.\begin{aligned}\theta &= \frac{k\Theta_0}{\sqrt{\{(E+k)-I\omega^2\}^2+R^2\omega^2}}\sin(\omega t-\phi)\\ &\equiv A\sin(\omega t-\phi)\\ \tan\phi &= \frac{R\omega}{(E+k)-I\omega^2}\end{aligned}\right\} \quad (3)$$

where A is the amplitude of motion of the inner cylinder induced by the sinusoidal torque of the suspension wire, and ϕ is the angle of phase difference between the motion at the top of the suspension wire and the forced oscillation of the inner cylinder. The amplitude ratio m is given by

$$m \equiv \frac{A}{\Theta_0} = \frac{k}{\sqrt{(E+k-I\omega^2)^2+R^2\omega^2}} \quad (4)$$

from Eq. 3, R and E are calculated as

$$\left.\begin{aligned}R &= \frac{kT\sin\phi}{2\pi m}\\ E &= k\left(\frac{\cos\phi}{m}-1\right)+\frac{4\pi^2 I}{T^2}\end{aligned}\right\} \quad (5)$$

where T is the period of oscillation ($\omega=2\pi\nu=2\pi/T$).

When two simple harmonic motions, i.e., the motion at the top of the suspension wire and the forced oscillation of the inner cylinder, whose directions of oscillation are at right angles to each other, are composed, the resulting Lissajous' figure is an ellipse as long as they are of the equal period. Let the area of an ellipse be S_e and that of the rectangle tangent to the ellipse be S_r. Then the next relation is known to hold.

$$\sin\phi = \frac{4}{\pi}\cdot\frac{S_e}{S_r} \quad (6)$$

The scheme of obtaining m and ϕ is realized by a mechanical and optical system. The dynamic viscosity η and the dynamic rigidity G are calculated from the observed R and E by the conventional formulae

$$\left.\begin{aligned}\eta &= \frac{R}{4\pi h}\left(\frac{1}{r_1^2}-\frac{1}{r_2^2}\right)\\ G &= \frac{E}{4\pi h}\left(\frac{1}{r_1^2}-\frac{1}{r_2^2}\right)\end{aligned}\right\} \quad (7)$$

where h, r_1 and r_2 are the length of the immersed portion of the internal cylinder, the radii of the internal and external cylinder, respectively.

Strictly speaking, the inertia effect of the sample which was discussed by S. Oka[5] can not be neglected. But in our present experiments, in which very low frequencies (long period of oscillation) were applied, the rigorous treatment taking into account the inertia of the sample is not necessary.

5) S. Oka et al., *Bull. Kobayashi Inst. Phys. Res.*, **3**, 9, 17 (1953).

The experimental condition was as follows: Three hardened steel wires, whose diameter ranged from 0.29 mm. to 0.90 mm. in accordance with the concentration of the sample solution, were used. Coaxial glass vessels of the outer diameter 9.386 cm., and inner one 5.905 cm., were used.

Mercury sulfosalicylate was prepared as follows[6]: An equivalent mass of yellowish mercuric oxide was mixed into the solution of commercial sulfosalicylic acid. When this mixture is heated in a water bath, flesh-colored mercury sulfosalicylate is obtained. The sample thus prepared, mixed with water, is boiled in a flask with reflux condenser for about an hour. After having been dissolved completely in water, it is poured into the space between the two cylinders, cooled and settled for two days in room temperature for conditioning.

The concentration of the solution was determined by evaporation, and was represented in weight per cent. The temperature of the sample to be tested was controlled at 20~65°C, by a water bath thermostat.

Results

Aging of the Solution.—As is usual in all colloidal solutions[7], the marked effect of aging in the physico-chemical properties is observed in our case. The solution of mercury sulfosalicylate, when it is newly prepared, appears as a transparent solution, but gradually loses its transparency and becomes a visco-elastic fluid. Fig. 1 shows the increase of the viscosity and modulus of the rigidity as a function of time.

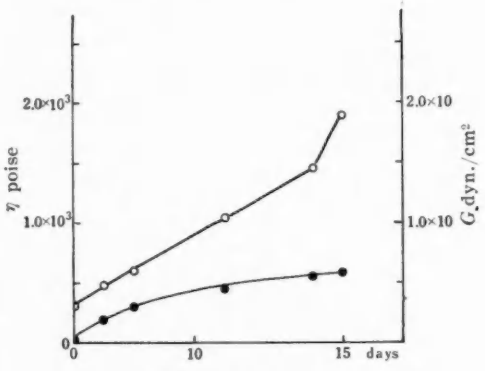


Fig. 1. Viscosity and rigidity of 3.16% mercury sulfosalicylate aq. solution vs. aging time. ○ indicates viscosity and ● rigidity.

6) For instance, J. Samejima, "Koshitsugaku (Colloid Science)", Shokabo, Tokyo (1949), p. 537.

7) For instance, C. Dittmar et al., *J. Poly. Sci.*, **18**, 275 (1955).

In our case of mercury sulfosalicylate solution, the viscosity increases rapidly in a few days, while the rigidity increases slowly. In the course of 10 or 15 days, rigidity seems to reach a saturation value, but viscosity continues to increase to a very large value.

Dependence on Frequency. — As is usually observed in the ordinary polymeric solutions, the dynamic viscosity and elasticity of the present system change with frequency.

Fig. 2 shows the viscosity and rigidity of 2.2% mercury sulfosalicylate solution, plotted against the period of oscillation (reciprocal frequency) from 8 sec. to 1286 sec. (about 22 min.). From this figure we see that, in a range of a short period, the viscosity decreases rapidly as the period of oscillation becomes shorter. But, when the period of oscillation is very long, it reaches a constant value.

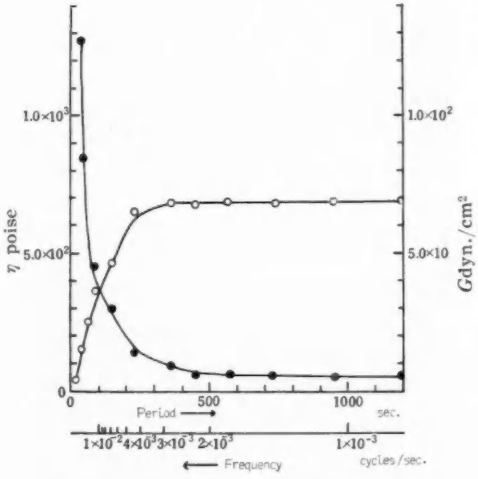


Fig. 2. Frequency dependence of viscosity η and rigidity G of 2.2% mercury sulfosalicylate aq. solution at 24°C. ○ indicates viscosity and ● rigidity.

On the other hand, the rigidity falls steeply in a range of short period. As the viscosity reaches to a certain constant value in a range of a long period, the rigidity also becomes constant. In other words, in a high frequency range, viscosity increases rapidly and rigidity decreases also steeply as the frequency becomes lower. And then, when the frequency is below 2.5×10^{-3} cycl./sec., viz., the period of oscillation is above 400 sec., both viscosity and rigidity are almost constant.

Dependence on Amplitude. — The amplitude effect is shown in Fig. 3, in which $\theta_{\max r=r_1}$ is the amplitude of the shear strain at the wall of the internal cylinder, as given by the following equation,

$$\theta_{\max r=r_1}=\left[\frac{2Ar_1^2r_2^2}{(r_2^2-r_1^2)r^2}\right]_{r=r_1}=\frac{2Ar_2^2}{r_2^2-r_1^2}$$

where A is the amplitude of the oscillation of the internal cylinder and r_1 or r_2 is the radius of the internal and external cylinder, respectively. In the present case, $\theta_{\max r=r}=3.316\ A$ ($r_1=2.953$ cm., $r_2=4.693$ cm.). The concentration of the sample is 1.58 wt. %, and the frequency of oscillation is kept constant. (In the present case, it is 1.29×10^{-1} cycl./sec.).

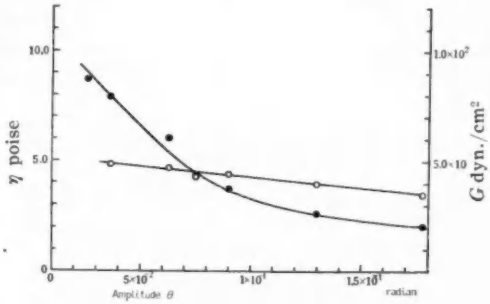


Fig. 3. Amplitude dependence of viscosity η and rigidity G of 1.58% mercury sulfosalicylate aq. solution. ○ indicates viscosity and ● rigidity.

It seems that the viscosity increases as amplitude decreases. But its gradient is fairly slight. As to the rigidity, on the other hand, the situation is somewhat different. It is large in the region of small amplitude, but decreases rapidly as the amplitude increases, and finally tends to a constant value. This is a noticeable experimental result. An explanation of this effect may be given by assuming a sort of structural breakdown by shear strain. An elastic structure breaks into a viscous flow process by a large deformation.

Effect of Concentration of Solution.—So long as we are concerned with dilute solutions, the rigidity seems to be proportional to the third power of concentration as is shown in Fig. 4. This result is in accord with that of agar-agar sol formerly reported[8].

8) T. Danno, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **72**, 1061 (1951).

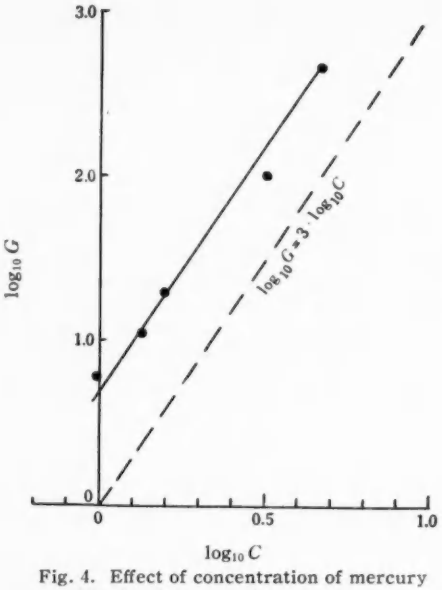


Fig. 4. Effect of concentration of mercury sulfosalicylate aq. solution.

Dependence on Temperature.—Both viscosity and rigidity decrease with the increase of temperature. Fig. 5 shows the results, where viscosity is plotted against the reciprocal of absolute temperature. The author has used the Andrade formula[9]

$$\eta = Ae^{\Delta E/RT}$$

to express the temperature sensitivity of viscosity η; A and ΔE were determined by the method of least square with regard to various periods of oscillation. Results are given in Table I. The apparent heat

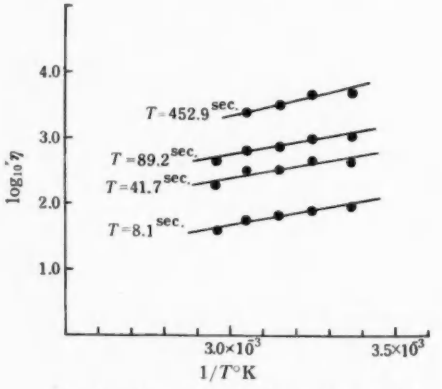


Fig. 5. Temperature dependence of viscosity.

9) E. N. da C. Andrade, *Phil. Mag.*, **17**, 497, 698 (1934).

TABLE I. CONSTANTS OF THE ANDRADE FORMULA

Period, sec.	$-\log A$	E, kcal.
8.1	−0.649	4.11
41.7	−0.210	3.96
89.2	−0.0147	4.10
452.9	−0.147	4.79

(For 4.53 wt. % solution).

of activation in relation to the viscous flow process is about 4 kcal./mol. This value makes one assume the existence of the cross-linking due to the weak secondary bonding like a hydrogen bond.

Discussion

From the results of frequency dependence, it is assumed that this solution has two mechanisms of relaxation. A mechanism which relaxes easily finishes its relaxation during the small period. When the period increases to a certain value, both viscosity and rigidity do not change with frequency due to the nearly complete relaxation of the first mechanism (Fig. 2). We have already seen that viscosity increases, while rigidity does not suffer a remarkable change in the course of aging (Fig. 1). An elastic scaffolding structure is formed in the first stage of gelation, and afterwards the gradual growth of suspending particles in a cavity follows. This is shown in the electron-micrograph

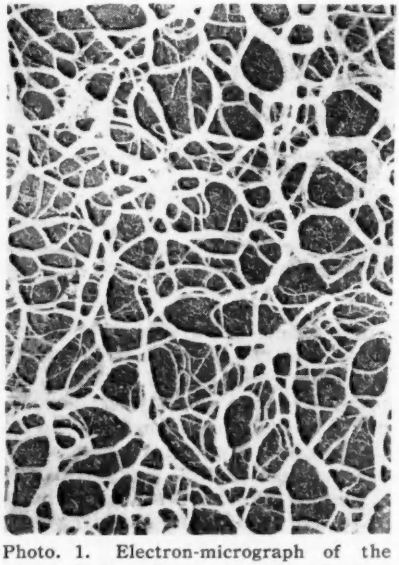


Photo. 1. Electron-micrograph of the aq. solution of mercury sulfosalicylate (×10,000).

(see Photo. 1). This means that the solution of mercury sulfosalicylate has a network structure of two phases.

As to the nature of cross-linking between these submicroscopic network structures, weak secondary bonding, for example, by hydrogenbond, is assumed, because the apparent activation energy of viscosity is calculated to be about 4 kcal./mol.

The author wishes to express his gratitude to Professor H. Akamatsu and Dr. T. Nakagawa both of the University of Tokyo for their leadership and encourgement throughout this investigation. It is also a pleasure to acknowledge the help of the members of Electron-microscope Laboratory of the University of Tokyo.

Department of Chemistry
Tokyo Gakugei University
Setagaya-ku, Tokyo

*Structural Heterogeneity in Viscose Fibers**

By Akiyoshi NAKAI

(Received February 23, 1959)

Though various theories as to the cause and nature of the skin-core effect in viscose fibers have been advanced, none seems to be entirely satisfactory to accout for all the facts so far observed. On the other hand, some observations have been presented which show that the actual structures are far more complicated than the skin-and-core model[1-5], but the results obtained are not yet conclusive.

Dyeing properties of the fiber sections have been studied by various workers, who have dealt almost exclusively with the differential staining of the skin and core. This phenomenon is, as Hermans[6] pointed out, due to a more rapid diffusion of the dye into the core than into the skin.

Generally, dyeing property has two major factors. These are dye diffusion velocity and dye equilibrium absorption. If the picture is oversimplified it would seem that the dye equilibrium absorption is connected with the total spatial per cent of amorphous areas but the dye diffusion velocity is connected with the size and distribution of amorphous areas or the average orientation of the chains in these areas. Then the structural factor which causes the differences in velocity of dye diffusion should not always be identified with that which causes the differences in equilibrium absorption of dye. This suggestion is proved in various experiments.

In addition to the dyeing property of fiber section based on diffusion velocity, therefore, the situation at sorption equilibrium should also be studied. As for this subject, an interesting contribution has been published by Hermans[6], but it seems that there is possibility of further study.

The present investigation is concerned with (1) the observation on the dyeing property of fiber sections and (2) a study of the radial structural gradient by a peeling-off method.

Dyeing Experiment of Fiber Sections

As is well known in ordinary dyeing, the amount of dye absorbed is not sensitively reflected to the depth of color shade beyond the range of fairly low degrees of absorption. In order to distinguish clearly a difference in depth of stained shade on the cross sections prolonged-dyed, dyeing should then be carried out with a diluted dye solution.

Cross sections mounted in the usual way on slides, were dyed for long periods at room temperature with Oxamine Blue 4R which was purified by chromatographing on silica gel.

* Presented before the Meeting of the Fiber Society of Japan, held at Osaka, May 16, 1957.

1) M. Horio et al., *Textile. Research J.*, **17**, 264 (1947).
2) R. L. Royer and C. Maresh, ibid., **17**, 477 (1947).
3) G. G. Taylor and J. C. Brown, *J. Soc. Dyers & Col.*, **69**, 396 (1953).
4) G. D. Joshi and J. M. Preston, *Textile Research J.*, **24**, 971 (1954).
5) K. Kato, *Science [Japan] (Kagaku)*, **25**, 41 (1955).
6) P. H. Hermans, *Textile Research J.*, **18**, 9 (1948).

Müller-bath-type Fiber.—The fiber used here was an ordinary rayon (No. 1) spun in a bath containing sulfuric acid 110 g./l., sodium sulfate 350 g./l., and zinc sulfate 15 g./l.

After half an hour of dyeing in a solution of 0.3% Oxamine Blue 4R to which 1% of sodium sulfate had been added, the cross section exhibited the differential staining of skin-and-core with a selectively stained core, as is well known already. This is shown in Fig. 1.

As the dyeing time increased, the intensity of the color increased over all the parts, especially at both the outer circumference of the skin and the boundary between skin and core. After prolonged dyeing—for example, after dyeing for 6 hr. the section showed a finer staining differentiation than the skin-and-core, as shown in Fig. 2. In the section, a narrow zone of the core next to the skin exhibited a darker shade than the central part and was separated from the latter by a rather sharp boundary, and then showed up as a dark band. Moreover, the outer circumference of the skin was seen to stain deeply, but this zone was so thin that it was difficult to distinguish its existence.

Even after further dyeing the above fine differentiation remained, although it was very difficult to distinguish the differences in depth of color shade because of the intensive staining over the whole section.

When such intensively dyed sections were washed with water, the stain was seen to bleed easily off the outermost thin zone and the core but to remain in the main part of the skin. After short washing, the clearness of the boundaries among the various zones became pronounced and the multilayer-like differential staining came again into view. Fig. 3 is a micrograph of such partially washed-out sections mounted in water. As to the phenomenon that by short washing a narrow zone of the core next to the skin became pronounced, drawing a dividing line from the central part, a similar fact was observed already by Hermans, who did not interpret this narrow zone as the differentiated layer different from the central part, but then explained that during washing the former discolored much later than the latter. On the basis of the above observations on both dyeing and washing, however, it seems rather reasonable to assume that the narrow zone has a much greater dye equilibrium absorption than the central part and that there is, moreover, no remarkable difference in velocity of dye diffusion between the two. In the swollen sections in Fig. 3, a very thin deeply-stained outermost zone seems to be seen, but not yet clearly.

When washing had been carried further, the dye disappeared completely from both the outermost thin zone and the core, and remained only in the main part of the skin. Fig. 4 is a micrograph of such a washed-out section after immersion in water, photographed with a contrasting light filter. There is no doubt that a very thin outermost layer exists actually at the outside of the skin, free from the refraction and diffraction effects associated with the cellulose/water interface, as shown previously by Preston and Joshi[7]. This thin outermost layer has a high velocity of dye diffusion and a great dye equilibrium absorption (proved in the next section) and then exhibits a similar property towards dyes as a narrow zone of the core next to the skin.

The above-mentioned phenomena were also observed in other Müller-bath-type fibers (see Fig. 5) and with other dyestuffs such as Sky Blue FF.

In Müller-bath-type fibers there are apparently four distinct layers which differ in dyeing property. The skin itself is composed of two layers which differ in dye equilibrium absorption, and so does the core. These are summarized in Table I.

TABLE I. DYEING PROPERTIES OF FOUR LAYERS IN MÜLLER-BATH-TYPE FIBER (in cross section)

Layer		Velocity of dye diffusion	Equilibrium dye absorption
Skin	1st layer	rapid	high
	2nd layer*	slow	low
Core	3rd layer	rapid	high
	4th layer	rapid	low

* The main part of the skin.

Skinless-type Fiber.—For a sample "Shintoramomen" (No. H-T) was used, which was a high tenacity rayon staple spun from low-alkali viscose in zinc-free and low-acid bath. Fiber of this type is marked by an all-skin structure, as shown in Fig. 6.

Fig. 7 shows a similar section washed-out after prolonged dyeing. In the section, the stain is seen to bleed completely off the outermost thin layer but to remain

7) J. M. Preston and G. D. Joshi, *Kolloid-Z.*, **122**, 6 (1951).

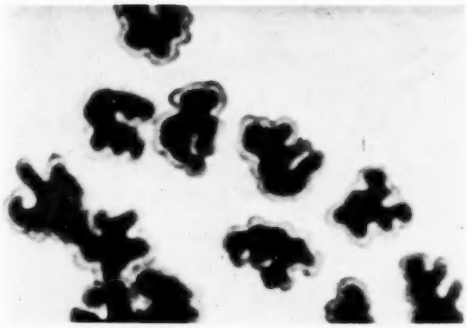


Fig. 1. Cross sections of an ordinary rayon (No. 1), dyed for 30 min. with Oxamine Blue 4R, mounted in canada balsam (×720).

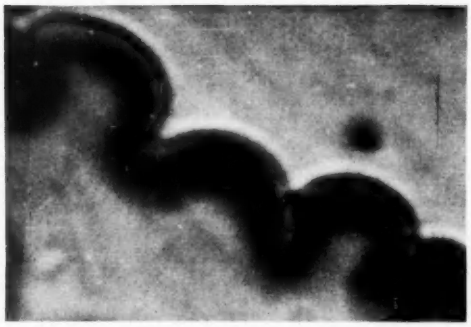


Fig. 4. Same as Fig. 3, except that washing was carried out further, whereas the dye was fixed only in the main part of the skin; mounted in water and examined by a oil-immersion objective (×2000).

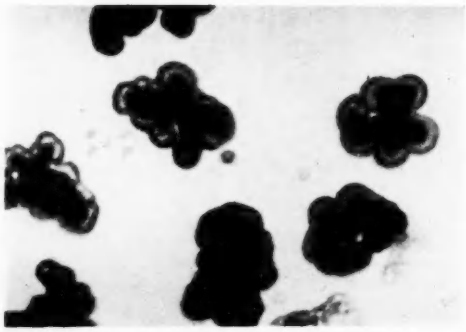


Fig. 2. Same as Fig. 1, except that the dyeing time was prolonged to 6 hr. (×900).

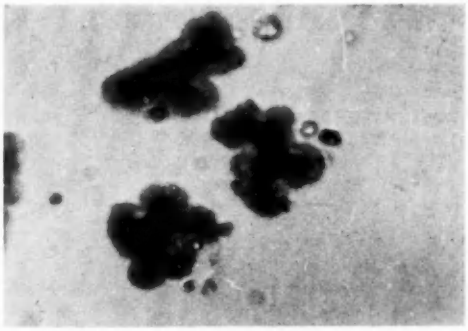


Fig. 5. Cross sections, of a tire-cord yarn, prepared as in Fig. 3 (×900).

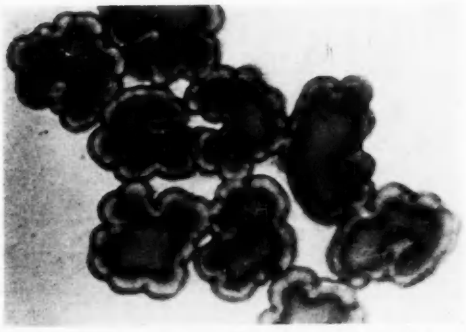


Fig. 3. Partially washed-out sections of an ordinary rayon (No. 1) pre-dyed intensively, mounted in water (×900).

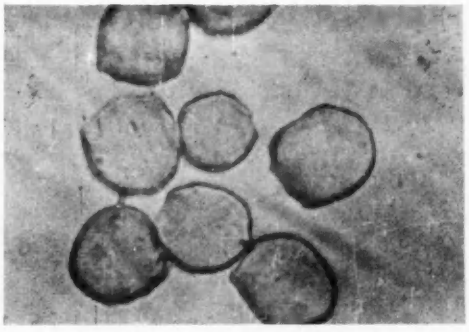


Fig 6. Cross sections of "Shintoramomen" (No. H-T), prepared as in Fig. 1 and mounted in canada balsam (×900).

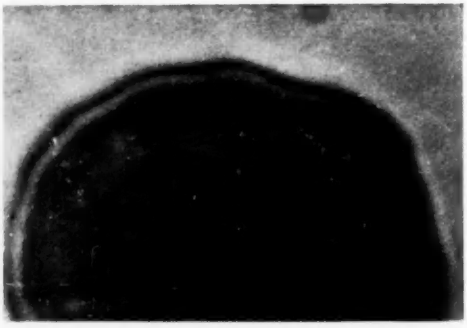


Fig. 7. Same fibre as in Fig. 6; section prepared as in Fig. 4 and mounted in water (×2000).

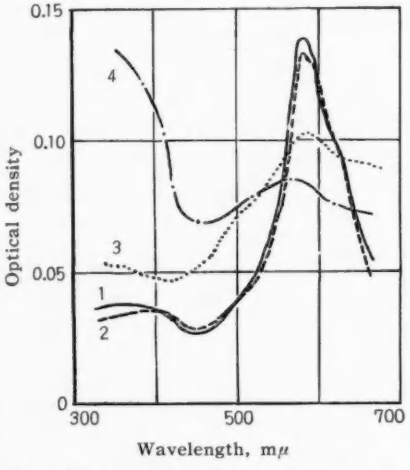


Fig. 8. Spectral sorption curves of dye solutions extracted from (1) the original fiber dyed with Japanol Brilliant Blue 6BKK, (2) the pre-dyed fiber peeled-off to *Pr* 0.23 (before nitration the pre-dyed fiber was vacuum-dried), (3) the pre-dyed fiber peeled-off to *Pr* 0.20 (before nitration the pre-dyed fiber was not vacuum-dried), and (4) the dyestuff decomposed by nitric acid.

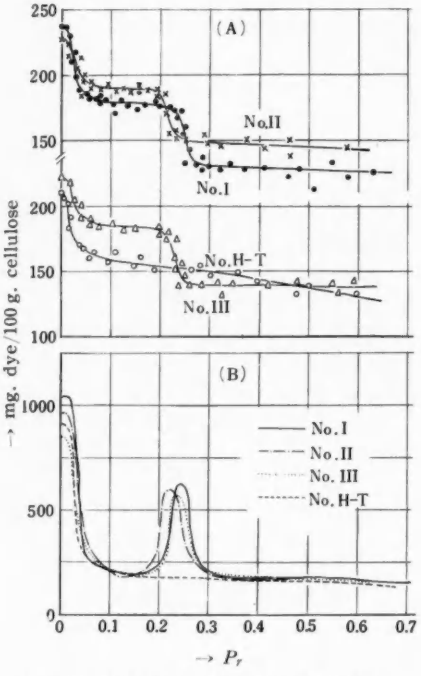


Fig. 9. (A) Amount of dye absorbed as a function of *Pr*. (B) Radial distribution curves in dye equilibrium absorption.

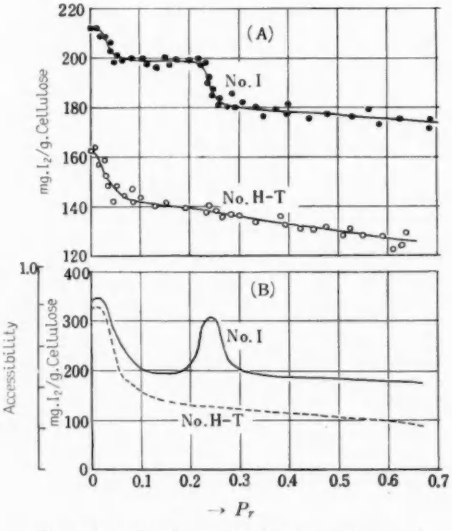


Fig. 10. (A) Amount of iodine absorbed as a function of P_r. (B) Radial distribution curves in iodine absorption and accessibility.

in the inner part, and then two distinct layers are clearly distinguishable. These two layers seem to correspond to the outermost and the second layer in the Müller-bath-type fiber, respectively.

Experiment with Peeling-Off Method

In view of the preceding observations it would seem that the actual structural heterogeneity is far more complicated than that assumed on the basis of the old skin-and-core model. In an investigation with peeling-off technique, therefore, it is necessary to peel the successive layers off as close as possible from the fiber surface toward the center and then to seek the nature of the radial structural gradient existing in fiber to the minutest details.

As a peeling-off technique the heterogeneous nitration presented by Okajima et al.[8] was applied. In a study of this kind, the point is in whether peeling-off is carried on successfully or not. Thereupon, numerous control experiments were carried out carefully.

Experimental Procedure.—A sample of fibers was thoroughly unraveled and vacuum-dried just before use (weight is W). Heterogeneous nitration was carried out at 18°C, and moisture was prevented from entering the reaction vessel. The nitration mixture was made from dry reagents and its composition was as follows:

Nitric acid (1.53)	3 g.	per 0.5 g. sample.
Acetic anhydride	3 g.	
Carbon tetrachloride	90 g.	

After nitrating the samples to the desired degree, they were washed enough with dry carbon tetrachloride, vacuum-dried and then treated with acetone for removing the nitrate layer.

After applying fresh acetone, they were washed with NH_4SH alcoholic solution recommended by Okajima for the removal of the residual nitrate groups from the fiber surface. Finally they were washed with water, vacuum-dried and weighed (W').

The degree of peeling-off (Pr) was given on the base of the original radius of the filament and obtained by $Pr=1-(W'/W)^{1/2}$.

In order to direct operations properly, microscopical examination of cross sections of the nitrated fibers was carried out using the staining technique. When nitration was carried on much longer, it was seen that the nitrated layer began to show more and more radial flaws, and that nitration proceeded in an irregular fashion. In order to avoid a drawback of this kind, the reaction time was limited to half an hour. If a greater degree of peeling-off was desired, the sample was peeled-off with acetone and then exposed a second time to the nitrating mixture.

Because of the necessity of studying a radial distribution of dye in the dyed fiber—this is the main object in the present investigation—the application of the above peeling-off method to the dyed sample was examined. Fig. 8 shows spectral sorption curves of the dye solutions extracted from the original and peeled-off predyed samples. This figure indicates that, if nitration proceeds under absolutely dry conditions, the dye which remains in the unreacted part has not been decomposed and the acid has not diffused into the inner part beyond the nitrated layer. It was found eventually that the dyed sample was peeled-off satisfactorily as well as the undyed sample. In this case, however, water should not be used for washing, because the dye absorbed in the unreacted part was dissolved away with water.

Samples.—The fibers selected for investigation were "Shintoramomen" (No. H-T) and three ordinary rayons (No. I—III). No. I—III were all spun in the same Müller bath; 1.5, 3.0 and 7.0, deniers, respectively.

Radial Distribution in Dye Equilibrium Absorption.—A sample was dyed to equilibrium at 25°C in a solution of 0.001% Japanol Brilliant Blue 6BKX to which 0.2% of sodium sulfate had been added, and washed briefly with water to remove the mechanically absorbed dye from the fiber surface, vacuum-dried and then peeled-off. In Fig. 9-A is given the amount of dye absorbed as a function of the degree of peeling-off. The radial distribution curves derived therefrom are shown in Fig. 9-B. These are in good agreement with the differential staining based on the differences in equilibrium absorption, irrespective of the differences in dyestuff and even in procedure of dyeing (Ref. Figs. 2, 3 and 7). The fact that a very thin outermost layer has a greater dye equilibrium absorption is experimentally proved here.

Radial Distribution in Crystallinity.—Using the Hessler and Power's method[9], the radial distribution in accessibility was first studied. In Fig. 10-A are given the amount of iodine absorbed on the fibers peeled-off to various degrees. The radial distribution curves derived therefrom are shown in Fig. 10-B, in which a ratio of the absorption value to 412** gives a value for the accessible fraction. Four layers in Müller-bath-type fiber and two in Shintoramomen are clearly distinguished also here.

The accessibility thus obtained is, however, due to the inner surface areas for absorption and seems to be an unsatisfactory measure for crystallinity. In order to seek conclusive evidence on the nature of the fine structure in each layer, the lateral-order (L.O.) distribution of each separated layer was further determined according to the hydrocellulose solubility method presented by Maeda[10]. For example, the L.O. of the outermost layer of No. 1 (P_r: 0∼about 0.05) was determined by calculation from the L.O. of the original fiber and the observed L.O. of the fiber peeled-off to 0.05 (the outermost layer just about

8) S. Okajima et al., This Bulletin, **26**, 322 (1953).

9) V. J. Hessler and R. E. Power, *Textile Research J.*, **24**, 822 (1954).

** The milligram of iodine absorbed per gram of methocel, as the sample of the completely amorphous cellulose.

10) K. Maeda, *J. Soc. Text. Cellulose Ind. Japan* (*Sen'i-Gakukai-shi*), **12**, 10 (1956).

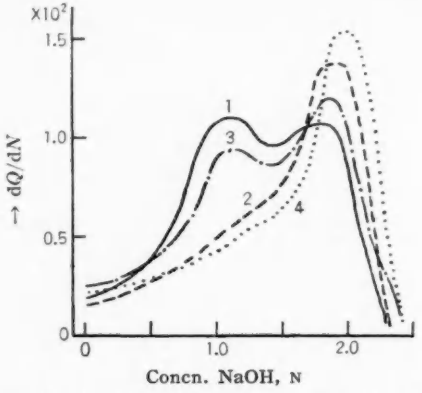


Fig. 11. L.O. distribution curves of each layers in No. No. 1.
(1) The outermost layer (P_r: 0～ca. 0.05). (2) The second layer (P_r: ca. 0.05～ca. 0.20). (3) The third layer (P_r: ca. 0.20～ca. 0.28). (4) The fourth layer (P_r: ca. 0.28～).

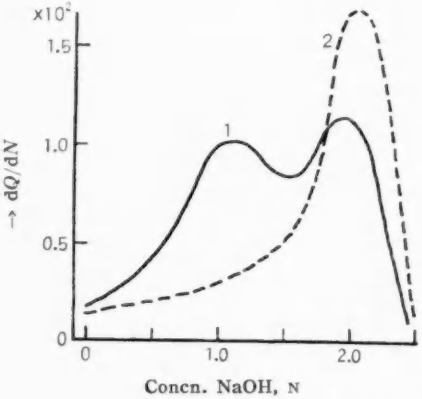


Fig. 12. L.O. distribution curves of each layers in No. H-T.
(1) The outermost layer (P_r: 0～ca. 0.05). (2) The second layer (P_r: ca. 0.05～).

removed). The results are shown in Figs. 11 and 12.

As is seen in the figures, there is an intrinsic difference in L.O. distribution between a layer with greater dye equilibrium absorption and that with less dye equilibrium absorption. The former has two peaks in its distribution curve and, consequently, lower crystallinity. The latter, on the other hand, gives only one peak in the region of considerably high order and, consequently, higher crystallinity. These are in agreement with the information obtained from the radial distribution in iodine absorption described before.

Discussion

As is seen from the above observations, there are two types of differentiated layers.

One is a layer rich in disordered material which shows a lower crystallinity and a greater dye equilibrium absorption. Cellulose gel of this type, which will be termed here "α-type", is formed by a momentary gelatinizing action, such as that of zinc ions[11].

The other is a highly crystallized layer with relatively limited amorphous regions and shows less dye equilibrium absorption. Cellulose gel of this type, which will be termed "β-type", is formed by a relatively slow gelatinizing action, such as those of sodium or hydrogen ions[11].

Consequently, it seems reasonable to assume that viscose fibers consist of the alternative succession of the α-type and β-type layers. In the Müller-bath-type fiber there are four successive layers, i.e., the α_1-, β_1-, α_2- and β_2-layer; the α_1- and β_1-layer altogether correspond to the skin, and the α_2- and β_2-layer to the core. This seems to be in agreement with the result of Joshi and Preston[4], who observed four zones which differ in transverse orientation.

As to the layer succession, there are some interesting facts as follows: (1) Fiber spun in a zinc-free bath has only one combination of the α-type and β-type layer, but fiber spun in a zinc-containing bath has double combinations. (2) The periods of the layer succession are identical in all fibers spun in the same composition of bath, irrespective of the differences of their deniers. These facts seem to lead to the suggestion that the bath composition is of essential importance for the occurrence of the Liesegang-like periodic coagulation which influences the rate of primary gelatination and, consequently, the degree of crystallization.

Moreover, all types of fiber have the outermost thin α-type layer, which will be designated "the cuticle layer"***, irrespective of the existence of zinc salt in their spinning bath. The formation of this layer seems to connect with some inevitable effect occurring when viscose contacts with bath liquid, — maybe, a momentary dehydration carried out in the

11) A. Nakai, ibid., **14**, 905 (1958); **15**, 9, 90, 166, 170 (1959).
*** The cuticle layer was shown also by Heyn, *Textile Research J.*, **27**, 449 (1957). Heyn's paper had not been published when the present investigation was presented at Spring Meeting of the Fiber Society of Japan, held on May 16, 1957.

order of the relaxation time of the macromolecules in viscose, on the surface of the extruded viscose[11].

The most noticeable conclusion to be drawn from the present study is that the main part of the skin has a good crystallinity as well as the central part. This is opposed to the opinions given in the majority of previous works, which maintain that the degree of crystallinity is less in the skin than in the core[12-14]. On the other hand, a few contributions have been reported which show that there is no remarkable difference in crystallinity between the two[15,16]. Since the actual differentiations are far more complicated as proved here, it is doubtful whether the actual nature of the structural heterogeneity can be sought by the methods used in previous works, for example, by a comparative study of the crystallinity of thick- and thin-skin fibers, or by that of the physical properties of fibers peeled-off to various degrees which kept a relatively long interval between the various ones.

The structural difference based on crystallinity is the major factor which causes the differences in dye equilibrium absorption, but not the major factor which causes the differences in velocity of dye diffusion. This is demonstrated by the following facts: (1) There is a remarkable difference in velocity of dye diffusion between the β_1- and β_2-layer, irrespective of the small difference in their crystallinities. (2) There is no difference in velocity of dye diffusion between the α_2- and β_2-layer, irrespective of the great difference in their crystallinities. Consequently, the skin-core effect is not, as Morehead and others believed, due to the differences in degree of crystallinity between the two.

As already shown by various works, the skin part has a higher degree of axial orientation than the core. Accordingly, the main part of the skin (the author's β_1-layer) seems to have a denser structure with good orientation and good crystallinity. The difficulty of the dye permeating into the main part of the skin, and, more generally, the skin effect seems probably to be due to the interdependence of its higher orientation and higher crystallinity.

The course of fiber formation from viscose seems not to be so simple as to be suggested by previous theories. The present investigation seems to demonstrate that some as yet unknown peculiarity in the process of diffusion of the bath components into the viscose is mainly responsible for skin formation.

The author wishes to express his grateful acknowledgment to Professor I. Tachi of Kyoto University for his kind encouragement. He is also indebted to Messrs. S. Hiraoka and S. Omoto for their valuable assistance.

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Department of Agricultural Chemistry
Faculty of Agriculture
Kyoto University
Sakyo-ku, Kyoto

12) F. F. Morehead and W. A. Sisson, *Textile Research J.*, **15**, 443 (1945).
13) N. H. Chamberlain and M. P. Khera, *J. Textile Inst.*, **43**, T123 (1952).
14) T. Yurugi, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **58**, 27 (1955).
15) P. H. Hermans, *Textile Research J.*, **20**, 553 (1950).
16) I. Sakurada and Y. Nukushina, Meeting of the Research Institute of Artificial Fibers, Japan (Oct. 1956).

Infrared Spectrum of α-Aminoisobutyric Acid and the Assignment of the Vibrational Frequencies

By Masamichi TSUBOI and Tadao TAKENISHI

(Received March 3, 1959)

As has been shown in our previous papers[1,2], the infrared absorption measurement is an effective means for detecting differences in the molecular configurations of amino acids in different environments. In order to investigate further in detail such differences in the molecular configurations, it is necessary to know the vibrational mode for each of the bands given by these amino acids. For glycine[3] and DL-alanine[4], complete assignments of the vibrational modes have been made to the bands observed in the NaCl (and also KBr for glycine) region. This paper refers to another simple amino acid, α-aminoisobutyric acid. The vibrational frequencies observed in the solid state infrared spectra of this compound and its deuterated (ND_3^+) one, and also of its hydrochloride will be shown, and then, to all of these observed frequencies, approximate vibrational modes will be assigned on the basis of the results of analyses of normal vibrations made by previous authors for simpler molecules.

It may be worthwhile to point out here that, in these molecules (probably because of their branched-chain structures), the couplings between the skeletal stretching vibrations and the CH_3 or NH_3^+ rocking vibrations are not so strong as in alanine. Therefore, detailed discussions may be made on the couplings between the CH_3 rocking vibrations and the NH_3^+ rocking vibrations.

Experimental

The sample of α-aminoisobutyric acid was purified with active charcoal and repeated recrystallization from water. The deuterated product (ND_3^+) was obtained by dissolving the acid in D_2O and then by evaporating the solvent in vacuum. During the procedure, the D_2O and the acid were kept away from the atmospheric moisture by use of a dry box. By repeating the procedure twice an almost completely deuterated product, practically free from the NDH_2^+ and ND_2H^+ groups, was obtained. α-Aminoisobutyric acid hydrochloride was obtained by dissolving the free acid in concentrated aqueous solution of hydrochloric acid (1.1 equivalents) and was purified by recrystallization from aqueous alcohol.

The infrared absorption measurements were made with Nujol mulls, hexachlorobutadiene mulls, and KBr disks. The instruments used were a Perkin-Elmer 21 spectrometer equipped with an NaCl prism and a Hilger H800 spectrometer equipped with an NaCl prism or with a KBr prism.

Results

Infrared absorption curves obtained for α-aminoisobutyric acid and its deuterated product are shown in Fig. 1, and that for the hydrochloride in Fig. 2. The observed frequencies of the bands are listed in Table I, and are graphically shown in Fig. 3, with their intensities. As to assignments given in the table and Fig. 3, discussions will be given below.

Assignments of the Vibrational Frequencies of Trimethylacetic Acid

Before discussing the vibration frequencies of α-aminoisobutyric acid, considerations will be made on the frequencies of trimethylacetic acid, $(CH_3)_3CCOOH$, which is iso-electronic with α-aminoisobutyric acid cation, $\begin{matrix}NH_3^+\\ CH_3\\ CH_3\end{matrix}\!\!>\!C\text{-}COOH$, the NH_3^+ group of the latter being substituted by the CH_3 group in the former. The frequencies (in the region of 650~1800 cm^{-1}) of $(CH_3)_3CCOOH$, as read from Sadtler Standard Spectrum No. 6355*, are listed in Table II.

For comparison, the frequencies of *tert*-butyl chloride, as observed by Sheppard[5]

1) M. Tsuboi, T. Takenishi and Y. Iitaka, This Bulletin, **32**, 305 (1959).
2) M. Tsuboi and T. Takenishi, ibid., **32**, 726 (1959).
3) M. Tsuboi, T. Onishi, I. Nakagawa, T. Shimanouchi and S. Mizushima, *Spectrochim. Acta*, **12**, 253 (1958).
4) K. Fukushima, T. Onishi, T, Shimanouchi and S. Mizushima, ibid., **13**, 236 (1959).
5) N. Sheppard, *Trans. Faraday Soc.*, **46**, 527 (1950).
* See also reference 7.

are also given in the parallel column. The assignment of the frequencies of *tert*-butyl chloride was made by Nakagawa[6] with the result as given in Table II and Fig. 3.

The vibrational frequencies of trimethylacetic acid can be assigned readily by comparing the frequencies with those of *tert*-butyl chloride and by taking the characteristic frequencies of the carboxyl group[7] into consideration (see Table II and Fig. 3).

The frequencies, 1695, 1408, 1192 and 935 cm^{-1}, (shown in Fig. 3 by thick vertical lines) are assigned to four vibrations of the carboxyl group; i. e., 1695 cm^{-1} to the C=O stretching vibration, 1408 and 1192 cm^{-1} to two vibrations including the C–O stretching and the OH in-plane deformation, and 940 cm^{-1} to the OH out-of-plane deformation vibration. The frequency 865 cm^{-1} is assigned to the C–C (carboxyl) stretching mode, as 895 cm^{-1} in acetic acid dimer[8] or 846 cm^{-1} in acetic acid monomer[8]. All the other frequencies of trimethylacetic acid are correlated (see Fig. 3) with the frequencies of *tert*-butyl chloride, although provisos should be added as follows: The CH_3 degenerate deformation frequency 1460 cm^{-1} in the latter splits into two, 1479 and 1456 cm^{-1}, in trimethylacetic acid. The CH_3 symmetric deformation frequency 1370 cm^{-1} in *tert*-butyl chloride is lowered to 1359 cm^{-1} in trimethylacetic acid; $C\begin{smallmatrix}C\\C\\C\end{smallmatrix}$ asymmetric stretching frequency 1240 cm^{-1} is raised to 1295 cm^{-1}, and the symmetric stretching frequency 812 cm^{-1} lowered to 766 cm^{-1}. This lowering and raising is explained as the result of interactions of the vibrations of the $(CH_3)_3$–C group with the vibrations of the carboxyl group, interactions between the 1359 and 1408 cm^{-1} vibrations, between 1295 and 1192 cm^{-1} vibrations, and between 766 and 865 cm^{-1} vibrations. The band due to the CH_3 rocking vibration observed at 910 cm^{-1} in *tert*-butyl chloride is probably obscured in trimethylacetic acid by the strong band at 935 cm^{-1}.

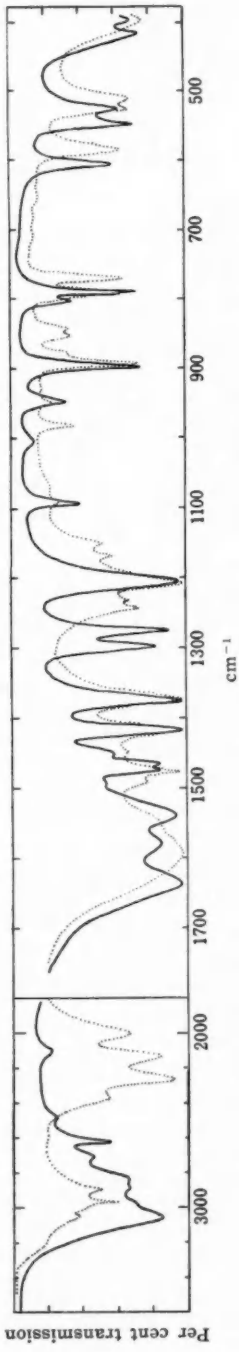

Fig. 1. Infrared absorption spectra of α-aminoisobutyric acid (——) and α-aminoisobutyric acid—ND_3 (·····).

6) I. Nakagawa, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **77**, 602 (1956). Nakagawa based his assignment (somewhat different from Sheppard's assignment) on his series of theoretical investigations of the normal vibrations of the molecules with the CH_3 groups and on the comparisons of the frequencies with those of other related molecules such as $CH(CH_3)_3$, etc.

7) D. Hadzi and N. Sheppard, *Proc. Roy. Soc.* (*London*), **A216**, 247 (1953).

8) J. K. Wilmshurst, *J. Chem. Phys.*, **25**, 1171 (1956).

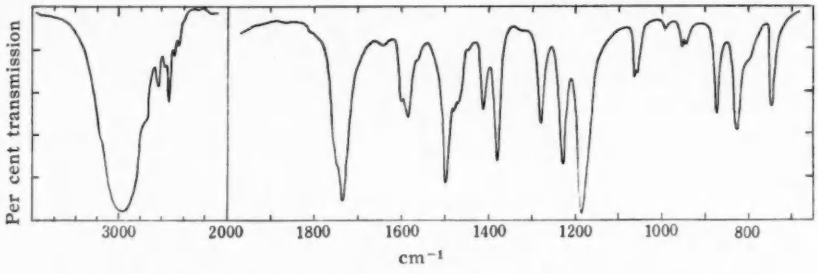

Fig. 2. Infrared absorption spectrum of α-aminoisobutyric acid hydrochloride.

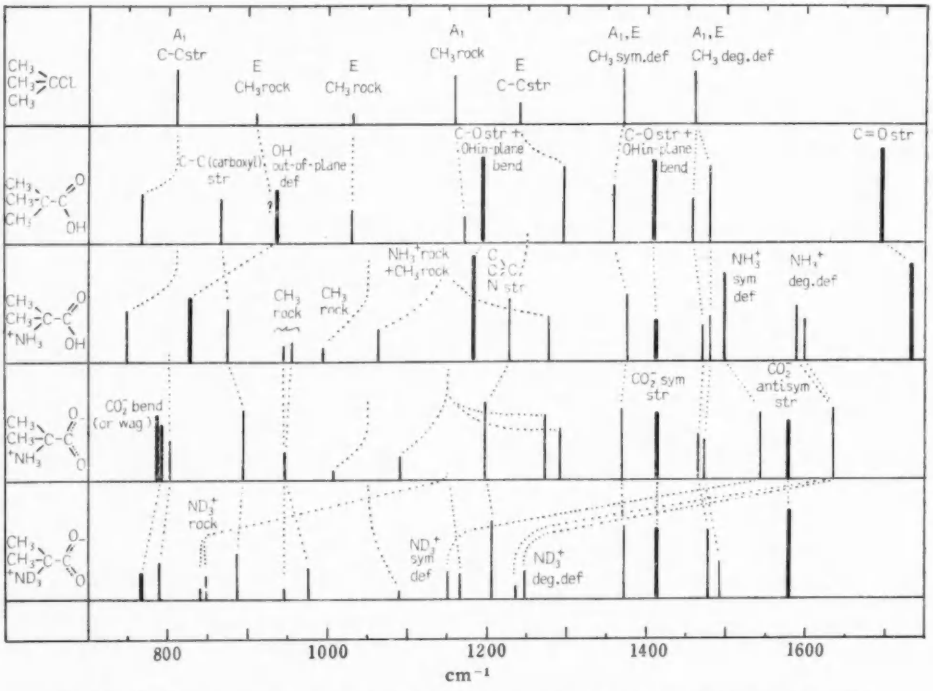

Fig. 3. Positions and intensities of the absorption bands of α-aminoisobutyric acid and related compounds.

Assignments of the Vibrational Frequencies of α-Aminoisobutyric Acid, its Deuterated (ND_3^+) Product, and its Hydrochloride

In the three crystals in question, α-aminoisobutyric acid, its deuterated product, and its hydrochloride, the molecules take the structures expressed by the formulae: $NH_3^+C(CH_3)_2COO^-$, $ND_3^+C(CH_3)_2COO^-$ and $NH_3^+C(CH_3)_2COOH$, respectively. These may be referred to in the following discussions as the zwitterion, the deuterated zwitterion, and the cation, respectively. In all of these three ions there seems to be no strong coupling between the four types of vibrations: the vibrations of the carboxyl group, the skeletal stretching vibrations, the hydrogen deformation vibrations (NH_3^+ and CH_3^+ deformation vibrations), and the hydrogen rocking vibrations. Discussions will, therefore, be presented below of these four types of vibrations in separate paragraphs.

A) Vibrations of the Carboxyl Group (shown in Fig. 3 by thick vertical lines).—In the cation, the carboxyl group takes the form,

TABLE I. OBSERVED FREQUENCIES (cm^{-1}) OF α-AMINOISOBUTYRIC ACID, ITS DEUTERATED PRODUCT (ND_3^+), AND ITS HYDROCHLORIDE, WITH THEIR ASSIGNMENTS
(s: strong, m: medium, w: weak)

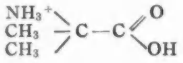		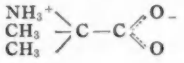		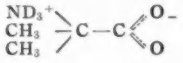		Assignment
~3000						OH str.
2630 2570 2535 2490 2440		3035 2875 2820 2690 2610 2480 2100				NH_3^+ and CH_3 str.
				2962		CH_3 deg. str.
				2889		CH_3 sym. str.
				2367 2262 2112 2043 1990		ND_3^+ str.
1732	s					C=O str.
1599 1587	s s	1635	s	1237 1247	w w	NH_3^+ or ND_3^+ deg. def.
		1578	s	1580	s	CO_2^- antisym. str.
1495	s	1544	m	1151	m	NH_3^+ or ND_3^+ sym. def.
1480 1470	m m	1473 1465	m m	1492 1478	m s	CH_3 deg. def.
		1413	s	1415	s	CO_2^- sym. str.
1411	m					C-O str.+OH in-plane def.
1376	s	1370	s	1373	s	CH_3 deg. def.
1277	m	1293 1273	s s	849 842	m w	NH_3^+ or ND_3^+ rock.
1229	s	1199	s	1206	s	asym. str.
1183	s					C-O str.+OH in-plane def.
1064 994	m w	1091 1008	w w	1167 1090	m w	CH_3 rock.
955 945	w w	946	w	976 947	m w	CH_3 rock.
875	m	895	s	888	s	C-C (carbonyl) str.
828	s					OH out-of-plane def.
748	m	803	m	790	m	sym. str.
↑		792 787	m s	768	m	CO_2^- bend. (or wag.)
		602	m	587	m	CO_2^- wag. (or bend.)
not observed		547 531	m m	529 519	m m	CO_2^- rock.
↓		430 407	m m	404	m	skeletal def.

TABLE II. ASSIGNMENTS OF THE FREQUENCIES (cm^{-1}) OF *tert*-BUTYL CHLORIDE AND TRIMETHYLACETIC ACID
(s: strong, m: medium, w: weak, b: broad)

$(CH_3)_3C-Cl$		$(CH_3)_3C-C(=O)OH$		Assignment
		1695	sb	C=O stretching
1460	s	1479	s	CH_3 deg. def.
		1456	m	
		1408	m	C-O str.+OH in-plane def.
1370	s	1359	m	CH_3 sym. def.
1240	m	1295	sb	C-C str. (E)
		1192	sb	C-O str.+OH in-plane def.
1159	s	1170	w	CH_3 rock. (A_1)
1031	w	1029	m	CH_3 rock. (E)
		935	sb	OH out-of-plane def.
910	w	masked ?		CH_3 rock.
		865	s	C-C (carboxyl) str.
812	m	766	s	C-C str. (A_1)

$C(=O)OH$ The bands due to the vibrations of this group are picked out on account of their frequencies, intensities, or breadth. These are at 1732 (C=O stretching), 1411 (C-O stretching + OH in-plane deformation), 1183 (C-O stretching + OH in-plane deformation), and 828 cm^{-1} (OH out-of-plane deformation).

The frequency of the last vibration is much lower than that (930 cm^{-1}) of carboxylic acids without the NH_3^+ group. This is also the case for glycine hydrochloride and DL-alanine hydrochloride. This fact may be understood, if we assume that the carboxyl groups in amino acid hydrochlorides are in different hydrogen bondings from those of the carboxylic acids containing no NH_3^+ groups; in the latter the ring dimer is mostly formed through the two OH·····O=C bondings, while in the former the NH_3^+ group, a strong proton donor, interrupts the hydrogen bondings in the ring dimer.

In the zwitterion and the deuterated zwitterion, the carboxyl group takes the form, $C(=O)O$ The antisymmetric and symmetric stretching vibrations of this group are observed around the usual positions, 1600 and 1400 cm^{-1},— 1578 and 1413 cm^{-1} in the undeuterated zwitterion, and 1580 and 1415 cm^{-1} in the deuterated zwitterion.

The COO^- rocking vibration has the frequency 504 cm^{-1} in glycine[3], and 540 cm^{-1} in DL-alanine[9]. Therefore, the band at 540 cm^{-1} (doublet with the peaks at 547 and 531 cm^{-1}) in the zwitterion of α-aminoisobutyric acid is assigned to the COO^- rocking vibration. In the deuterated zwitterion, the band at 520 cm^{-1} is picked up as the corresponding one.

The COO^- bending and wagging vibrations have the frequencies 607 and 694 cm^{-1} respectively in glycine[3]. According to the result of the calculation of the normal vibrations in alanine by Fukushima[10], the COO^- bending frequency must be much higher than 607 cm^{-1}, and the band at 746 cm^{-1} was assigned to this vibration. The COO^- wagging vibration in this molecule was assigned to the band at 642 cm^{-1}. α-Aminoisobutyric acid gives two strong bands at 602 cm^{-1} and 790 cm^{-1} (doublet with the peaks at 792 and 787 cm^{-1}) in the region 600~800 cm^{-1}. By analogy with the case of DL-alanine, the band at 602 cm^{-1} is tentatively assigned to the COO^- wagging vibration and that at 790 cm^{-1} to the COO^- bending vibration.

A difficulty of this assignment is due to the fact that, very close to by the band at 790 cm^{-1}, there is another band observed at 805 cm^{-1}, which is later shown to be assigned to the $C-C(-N^+)-C$ symmetrical stretching vibration. The two vibrations, COO^- bending and $C-C(-N^+)-C$ symmetrical stretching, with dipole oscillations in almost the same direction, would couple strongly, so that the two bands due to these two

9) M. Tsuboi, to be published.

10) K. Fukushima, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **79**, 370 (1958).

vibrations appear much more apart from each other. From this point of view, the band at 790 cm^{-1} is notlikely due to the COO^- bending vibration. Therefore another choice to assign the 790 cm^{-1} to the COO^- wagging and the 602 cm^{-1} to the COO^- bending is not entirely eliminated.

B) Skeletal Stretching Vibrations. — The skeletal stretching frequencies of the structure are expected to be close to those of the structure (see above), the symmetrical one being expected to be around 800 cm^{-1} and the asymmetrical one around 1200 cm^{-1}.

Actually, however, a band in the cation that may be assigned to the symmetrical stretching vibration is observed at 748 cm^{-1}, a little lower than 800 cm^{-1}. This is attributed to a lowering of the frequency of the vibration in question due to its coupling with the C–C (carboxyl) stretching vibration. The band that may be assigned to the C–C (carboxyl) stretching vibration is observed at 875 cm^{-1}, a little higher than usual (835 cm^{-1} in trichloroacetic acid dimer[7]) just as is expected from the above-mentioned coupling of the two vibrations.

In the zwitterion, the C–C (carboxyl) stretching frequency is 895 cm^{-1}, a little higher than in the cation; and the symmetrical stretching frequency is 803 cm^{-1}, a usual value.

The band of the cation at 1229 cm^{-1} and that of the zwitterion at 1199 cm^{-1} are assigned to one of the asymmetrical stretching vibrations**.

In the deuterated zwitterion, the three skeletal stretching frequencies, namely, the symmetrical and asymmetrical stretching frequencies of the structure and the C–C (carboxyl) stretching frequency, are found to be 790, 1206 and 888 cm^{-1}, respectively.

C) NH_3^+, ND_3^+ and CH_3^+ Deformation Vibrations.—As to the assignments of these vibrations, the results of studies on the vibrations of the glycine molecule[3] as well as of some simple molecules with the CH_3 group[11] are to be referred to. In the cation, the NH_3^+ degenerate deformation vibration is assigned to the doublet with the peaks at 1599 and 1587 cm^{-1}, and the NH_3^+ symmetric deformation vibration to the strong band at 1495 cm^{-1}. In the undeuterated zwitterion, the bands corresponding to the above two are at 1635 and at 1544 cm^{-1} respectively, 30~50 cm^{-1} higher than in the cation. This difference in the positions of bands may be explained by considering that the intermolecular (interionic) hydrogen bonding is stronger for the zwitterion than for the cation.

In the deuterated zwitterion, the doublet with peaks at 1237 and 1247 cm^{-1} and the band at 1151 cm^{-1} are interpreted as corresponding to the above two bands. Then, the factors of the shiftings of these bands are respectively 1.32 and 1.34, in agreement with the expected values, 1.37 and 1.31, respectively.

CH_3 degenerate deformation is assigned to a doublet around 1470 cm^{-1} and CH_3 symmetric deformation to a band near 1370 cm^{-1} in any of the cations, the undeuterated zwitterion, and the deuterated zwitterion.

D) NH_3^+, ND_3^+ and CH_3 Rocking Vibrations.—In any of the above three ions now under discussion, six rocking vibrations are expected, two from the NH_3^+ (or ND_3^+) group and four from the two CH_3 groups. In glycine, both of the two NH_3^+ rocking vibrations are observed in the vicinity of 1150 cm^{-1} [3]; and in isopropyl chloride, the four CH_3 rocking vibrations are observed at 1160, 1062, 949 and 932 cm^{-1} [10]. The location of the bands corresponding to the six rocking vibrations may be made around these frequencies.

Actually, in the cation, there are two weak bands observed, at 955 and 945 cm^{-1}, and these may correspond to the above two frequencies at 949 and 932 cm^{-1} of isopropyl chloride. Instead of bands around 1160 and 1062 cm^{-1}, however, three bands are observed at 1277, 1064 and 994 cm^{-1}. This fact may be explained as a result of interactions of the CH_3 rocking and the NH_3^+ rocking vibrations; thus, the two CH_3 rocking frequencies, originally at 1160 and 1062 cm^{-1} are lowered respectively to 1064 and 994 cm^{-1} and the two

** Only one band could be observed though two are theoretically expected.

11) I. Nakagawa and S. Mizushima, This Bulletin, 28, 589 (1955).

NH_3^+ rocking frequencies, originally around 1150 cm^{-1} are both raised to 1277 cm^{-1}.

In the undeuterated zwitterion, a band with a medium intensity is observed at 946 cm^{-1}. This band is considered to be an unresolved doublet and to correspond to the two CH_3 rocking vibrations observed at 949 and 932 cm^{-1} in isopropyl chloride and at 955 and 945 cm^{-1} in the α-amino-isobutyric acid hydrochloride. Besides this, four bands are observed at 1008, 1091, 1273 and 1293 cm^{-1}. These four bands are again explained as resulting from interactions of two of the four CH_3 rocking vibrations with the two NH_3^+ rocking vibrations, all of which are considered to be originally in the vicinities of 1160 and 1062 cm^{-1} (see Fig. 3).

This explanation is supported by what was observed of the rocking vibrations in the deuterated zwitterion. In the deuterated zwitterion, in which the NH_3^+ group is substituted by the ND_3^+ group, the above-mentioned interactions between the CH_3 and NH_3^+ rocking vibrations should be absent, and hence, the almost pure CH_3 rocking vibrations are expected to occur in the vicinities of 1160 and 1062 cm^{-1}. Actually, two bands are observed at 1167 and 1090 cm^{-1} in the deuterated zwitterion. It is also expected from the above explanation, that the two ND_3^+ rocking vibrations occur around $1160/1.32 = 880$ cm^{-1}. Actually, two bands are observed at 849 and 842 cm^{-1}. The observed frequencies of the bands are sufficiently close to the expected ones to support the above explanation.

Going into detail, however, the observed frequencies of the two CH_3 rocking vibrations are somewhat higher, and those of the two ND_3^+ rocking vibrations are somewhat lower, than the corresponding expected frequencies. This fact suggests that there are interactions of another type between the CH_3 and ND_3^+ rocking vibrations.

Corresponding to the other two CH_3 rocking vibrations in the deuterated zwitterion, expected around the 940 cm^{-1}, two bands are actually observed at 976 and 947 cm^{-1}. That the band at 976 cm^{-1} is situated at a little higher position than the expected position, 940 cm^{-1}, may again be attributed to the interactions of the CH_3 and ND_3^+ rocking vibrations***.

We wish to express our sincere thanks to Professor San-ichiro Mizushima, Dr. Takehiko Shimanouchi and Dr. Haruomi Oeda for their kind encouragement and valuable suggestions and to Miss Chie Yamazaki for helpful assistance.

Department of Chemistry
Faculty of Science
The University of Tokyo
Hongo, Tokyo (M. T.)

Central Research Laboratory
Ajinomoto Co., Inc.
Kawasaki, Kanagawa (T. T.)

12) N. Sheppard, *Trans. Faraday Soc.*, **46**, 533 (1950); G. Radinger and H. Wittek, *Z. physik. Chem.*, **B45**, 329 (1940); I. Nakagawa, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **77**, 602 (1956).

*** Under the assumption that all the rocking vibrations are independent of vibrations of other kinds in the zwitterion and in the deuterated zwitterion, the assignment, above made, of the six rocking frequencies is almost consistent with the product rule. Thus, the observed ratio, $1293\times1274\times1091\times1008\times946\times946/849\times842\times1167\times1090\times976\times947=1.93$, is close to the calculated ratio, 1.81. However, it is to be noted that the observed and calculated ratios are not in complete agreement. This is probably to be explained by considering that the assumption is not entirely valid, in other words, that some other vibrations, e. g., CH_3, NH_3^+, or ND_3^+ degenerate deformation vibrations and C-N stretching vibrations are coupling a little with the rocking vibrations.

Infrared Spectra of Salicylaldehyde, Methylsalicylate and their Sodium Compounds

By Haruka YAMADA

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Concerning the infrared spectra of conjugated chelate compounds, it is well known that the absorption bands associated with the OH stretching and the C=O stretching vibrations show some peculiarities that are not observed in the spectra of the usual hydrogen-bonded molecules.

The formation of the intramolecular hydrogen bond in conjugated chelate compounds may be mainly due to electrostatic and charge transfer forces. Though some interpretations of the spectra, common to various conjugated chelate compounds, have been given by considering resonance structures, a question as to what structure contributes predominantly to the resonance has not yet been solved completely. The important contribution of ionic structure to the resonance was pointed out by some investigators[1], based on the infrared studies of the C=O bands, while the ionic structure was disregarded by a few others[2] from the measurements of the OH bands. The OH band seems to be inappropriate for accurate measurement because of its broad band width. The intensity measurement of the C=O band has not yet been made. In these circumstances, more experimental knowledge is required to make an analysis of this problem. Salicylaldehyde and methylsalicylate are suitable for the intensity measurements of the C=O bands and for the present analysis.

The sodium compounds of salicylaldehyde and methylsalicylate are very interesting, because they are expected to have an intermediate character between salts and metal chelate compounds and further will be closely related to the hydrogen-bonded compounds. The measurements for these compounds, therefore, will not only make their structures clear but also give a valuable item of knowledge in regard to the hydrogen-bonded chelation.

Experimental

Measurements were made by a Perkin-Elmer Model 112 Infrared Spectrophotometer equipped with CaF_2 and NaCl prisms. For dilute solutions, fixed cells of 0.01, 0.05 and 1 cm. thicknesses were used, and the thicknesses of the thin cells were determined by the interference method. The slit widths for intensity measurements were kept constant and ranged from 0.07 to 0.15 mm. The integrated absorption intensity of a band, A ($mol^{-1}\cdot l.\cdot cm^{-2}$) was calculated by the following formula;

$$A = (K/Cl)\cdot \Delta\nu_{1/2}\cdot \ln(I_0/I)_{max}$$

where C, l, $\Delta\nu_{1/2}$ and $\ln(I_0/I)_{max}$ have their usual meanings and K is obtained from Ramsay's table[3], by use of the spectral slit width calculated by Kudo's equation[4].

The samples used were purified by distillation. The boiling points were as follows; 68.8~69.0°C/10 mmHg for salicylaldehyde, 73.0~73.5°C/5 mmHg for methylsalicylate and 51.0~51.2°C/9 mmHg for benzaldehyde. *o*-Methoxybenzaldehyde was prepared from salicylaldehyde and dimethylsulfate[5]. The boiling point was 37.3~38.0°C.

The sodium compounds of salicylaldehyde and methylsalicylate were prepared by mixing an excess of salicylaldehyde and methylsalicylate with ethylalcoholate[6]. The sodium compound of methylsalicylate was also prepared by throwing metallic sodium into methylsalicylate. Upon heating, the sodium compound of salicylaldehyde chared at ca. 250°C instead of melting and the sodium compound of methylsalicylate at ca. 180°C. From the titration with hydrochloric acid, it was determined that each compound contained two molecules of salicylaldehyde or methylsalicylate for a sodium ion.

Results and Discussion

The results for the C=O bands of salicylaldehyde and methylsalicylate in

1a) R. S. Rasmussen, D. D. Tunnicliff and R. R. Brattain, *J. Am. Chem. Soc.*, **71**, 1068 (1949).
1b) D. Hadzi and N. Sheppard, *Trans. Faraday Soc.*, **50**, 911 (1954).
2a) M. Tsuboi, This Bulletin, **25**, 385 (1952).
2b) M-L Josein, N. Fuson, J-M Lebas and T. M. Gregory, *J. Chem. Phys.*, **21**, 331 (1953).
2c) H. Tsubomura, ibid., **24**, 927 (1956).
3) D. A. Ramsay, *J. Am. Chem. Soc.*, **74**, 72 (1952).
4) K. Kudo, *J. Spectroscop. Soc. Japan* (*Bunkō Kenkyū*), **9**, 36 (1954).
5) A. Kalschalowsky and St. v. Kostanecki, *Ber.*, **37**, 2347 (1904).
6) N. V. Sidgwick and F M. Bewer, *J. Chem. Soc.*, **127**, 2379 (1925).

TABLE I. THE C=O BANDS OF SALICYLALDEHYDE AND METHYLSALICYLATE IN CARBON TETRACHLORIDE

		ν_{max} cm^{-1}	Concn. mol.·l^{-1}	$\ln(I_0/I)_{max}$	$\Delta\nu_{1/2}$ cm^{-1}	$A\times10^{-4}$ mol^{-1}·l.·cm^{-2}
Salicylaldehyde	I	1668	0.0942	2.487	7.00	2.60
	II	1668	0.0449	1.276	6.75	2.66
	III	1668	0.0634	1.814	6.80	2.70
	average	1668				2.65
Methylsalicylate		1683	0.0879	1.663	13.6	3.56

TABLE II. THE FREE C=O BANDS AND THE INTERMOLECULAR HYDROGEN-BONDED C=O BANDS OF BENZALDEHYDE AND *o*-METHOXYBENZALDEHYDE IN CARBON TETRACHLORIDE

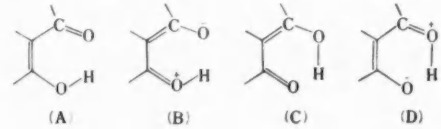
	ν_{max} cm^{-1}	$\Delta\nu_{1/2}$ cm^{-1}	$A\times10^{-4}$ mol^{-1}·l.·cm^{-2}
Benzaldehyde	1708	8.40	2.36
Benzaldehyde+*n*-butanol	1707	15.4	2.96
o-Methoxybenzaldehyde	1694	8.2	2.60*
o-Methoxybenzaldehyde+*n*-butanol	1693	13.2	3.25*

* The intensities are summed up for two ν_{max} assigned to its two isomers, though the intensity of one of them, at 1667 cm^{-1}, is very weak.

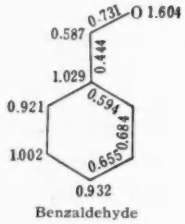
carbon tetrachloride solution are tabulated in Table I. In order to know whether or not the intensity of the band alters with chelating, the spectrum of salicylaldehyde should be compared with that of *o*-methoxybenzaldehyde, as the effect of the conjugation with the benzene ring and that of the ortho-substituted oxygen atom on their C=O groups are the same for both compounds. The results of the measurements for *o*-methoxybenzaldehyde[7] are shown in Table II. Because the intensity of the C=O band for salicylaldehyde is nearly equal to that for *o*-methoxybenzaldehyde, it comes out that the chelation effect does not alter the intensity. As the intensity of the C=O band for methylsalicylate shows the normal value of esters[8], it appears that the chelation effect has a large shift for the C=O stretching frequency towards lower frequency region but hardly affects the intensity. The lack of intensity change may indicate that the change in the bond moment is inappreciable.

In Table II are given the results for the conjugated C=O groups forming the intermolecular hydrogen bond with *n*-butanol. Here, the volume percentages of *n*-butanol in carbon tetrachloride range from 30 to 50%. Almost all the C=O groups of the compound in these solutions form the intermolecular hydrogen bond, since the frequency at the maximum absorption and the intensity of the band do not change with the concentration of *n*-butanol. By the formation of the intermolecular hydrogen bond the intensity noticeably increases, while the change in the frequency is very slight. These phenomena are different from those observed in the chelate compounds and can be explained by Tsubomura's theory[2e].

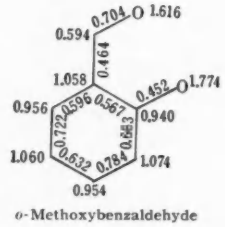
For the conjugated chelate compounds the four possible resonance structures shown below should be taken into account.



7) The ortho-substitution effect can be estimated by the comparison between benzaldehyde and *o*-methoxybenzaldehyde. The decrease of the frequcency and the increase of the intensity for the C=O band were observed by introducing the methoxy group. These changes are due to the migration of the lone pair electrons belonging to the oxygen atom and seem to be explained by the results expected from the molecular diagrams shown below. The molecular diagrams are calculated by a simple LCAO-MO method by use of Orgel's parameters.



Benzaldehyde



o-Methoxybenzaldehyde

8) G. M. Barrow, *J. Chem. Phys.*, **21**, 2008 (1953).

TABLE III. SOLVENT EFFECT ON THE C=O BANDS OF SALICYLALDEHYDE AND METHYLSALICYLATE

	Solv.	ν_{max} cm^{-1}	$\Delta\nu_{1/2}$ cm^{-1}	$A\times10^{-4}$ $mol^{-1}\cdot l.\cdot cm^{-2}$
Salicylaldehyde	chloroform	1666	9.3	2.60
	n-butanol	1667	8.8	2.52
	acetonitrile	1666	8.6	2.61
Methylsalicylate	chloroform	1678	19.8	4.16

TABLE IV. THE C=O BAND OF ENOL-FORM OF ACETYLACETONE IN CHLOROFORM

ν_{max} cm^{-1}	Concn. $mol.\cdot l^{-1}$	Enol* content %	$\Delta\nu_{1/2}$ cm^{-1}	$A\times10^{-4}$ $mol^{-1}\cdot l.\cdot cm^{-2}$
1615	0.103	78	62.8	9.15

* K. Kuratani, *Rept. Inst. Sci. and Technol., Univ. Tokyo*, **6**, 217 (1952).

By the formation of the chelate ring the C and D structures newly contribute to the resonance. The important contribution of the B structure was at first pointed out by Rasmussen et al.[1a] and afterwards by Hadzi et al.[1b] again, while the importance of the C structure was reported by Tsuboi[2a], Josein et al.[2b] and Tsubomura[2c]. As it may be true that for a molecule having the carbonyl group the change in ionic character of C=O bond on chelate bonding contributes to the intensity increase of the C=O band, there seem to be two possibilities to account for the present results. First, if the C structure makes a significant contribution to the structure of the chelating compounds, the bond order of the C=O group will decrease and the appreciable change in the bond moment of the group will not occur, in accord with the results. Secondly, if both the structures of B and D equally contribute to the resonance, an increase in the contribution of the B structure will give rise to a decrease of the bond order and hence to the decrease of the C=O frequency, and the equal contribution of both the structures will not significantly alter the bond moment of the C=O group, because the directions of the polarities of both the resonance structures are opposite, and will result in the unaltered intensity of the C=O band. The second interpretation, however, seems to be less reasonable than the first, because in the second the D structure, in spite of its high energy, must contribute to the resonance to the same extent as the increase of the B structure.

In a molecule having a polar resonance structure the per cent contribution of each structure may vary with the change of solvent. As for such a molecule, a slight change in the per cent contribution gives rise to appreciable changes in the dipole moment and in the intensity of the infrared absorption band. The intensity of the C=O band for salicylaldehyde is the same in carbon tetrachloride, in chloroform and even in acetonitrile. This fact indicates the important contribution of non-ionic structures in this molecule. The chelation in methylsalicylate is not so strong as in salicylaldehyde because of the ester resonance[9]. The contribution of the C structure to methylsalicylate, therefore, will be less important than the contribution to salicylaldehyde. In the case of methylsalicylate, the influence of polar solvent on the intensity of the C=O band was found.

As for β-diketones, conjugated chelate compounds take the enol forms. As the C=O bands of these compounds overlap with their C=C bands, the intensities of the bands appear to be very large. Rasmussen et al. described the fact that a very broad band, estimated to be more than a hundred times as strong as the normal carbonyl band, was observed in the range 1639~1538 cm^{-1}.

As is shown in Table IV, the integrated intensity of the broad band including the C=O and C=C bands measured for the enol form of acetylacetone is only about twice as strong as that of the usual conjugated aliphatic C=O band; e.g., the value for isophorone in chloroform is 4.6×10^4 $mol^{-1}\cdot l.\cdot cm^{-2}$. The interpretation for β-diketones will be essentially the same as that for salicylaldehyde. Since the normal value of the intensity of the C=O band for this molecule is expected, this fact indicates

9) A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds", Prentice-Hall, Inc., New York (1952), p. 164.

that the intensity of the C=C band increases by the chelation effect.

Concerning the band shapes for the chelate compounds, there can be found a relation between the C=O and the OH band. A compound having a sharp C=O band shows a broad OH band, and conversely a compound having a broad C=O band a sharp OH band. Strong chelation is accompanied by a sharp C=O and a broad OH band. Acetic acid is regarded as a sort of chelate compound. The C=O band measured in carbon tetrachloride solution is shown in Table VI. The association of acetic acid to the dimer is so strong that it dissociates with difficulty to the monomer even in 0.05 mol.·l^{-1} concentration. It is interesting to notice that the intensity of the C=O band seems to be normal, though this band is assigned to the antisymmetric stretching vibration caused by the coupling of the two C=O groups.

TABLE V. THE C=O BAND OF ACETIC ACID DIMER IN CARBON TETRACHLORIDE

ν_{max} cm^{-1}	Concn. mol.·l^{-1}	$\Delta\nu_{1/2}$ cm^{-1}	$A\times10^{-4}$ $mol^{-1}\cdot l.\cdot cm^{-2}$
1713.5	0.0481	10.4	3.92

TABLE VI. THE BAND SHAPES OF C=O AND OH STRETCHING VIBRATIONS

	C=O band	OH band
Salicylaldehyde	sharp	broad
Methylsalicylate	broad	sharp
Acetic acid dimer	sharp	broad

TABLE VII. THE WAVE NUMBERS FOR SALICYLALDEHYDE, METHYLSALICYLATE (IN LIQUID) AND THEIR SODIUM COMPOUNDS (IN NUJOL)

Salicylaldehyde	Sodium compound of salicylaldehyde	Methylsalicylate	Sodium compound of methylsalicylate
		701 w	701 w
715 m	731 m		712 m
766 s	766 s	759 s	758 m
	777 m		771 m
		800 m	801 w
		813 sh	806 w
		848 m	850 w
883 s	893 s	866 m	860 sh
		963 m	964 m
1023 m	1036 m	1032 m	1032 m
		1090 m	1085 m
1113 m	1119 s	1136 m	1148 sh
1149 m	1148 s	1158 m	1157 m
1182 s	1180 s	1195 m	1190 m
1201 sh			
1227 s	1246 s	1212 s	1213 s
1276 s	1279 m	1253 m	1257 m
		1301 s	1306 sh
1319 m	1315 m	1325 s	1316 s
		1439 s	1439 s
1577 w		1587 m	1540 m
1619 m	1600 m	1615 m	1607 w
1663 s	1680 s	1679 s	1682 s
3100 w	3344 m	3141 m	3206 m
			3351 m

The wave numbers of the infrared bands for the sodium compounds of salicylaldehyde and methylsalicylate observed in the solid state are tabulated in Table VII, together with the wave numbers for salicylaldehyde and methylsalicylate in the liquid state.

From the infrared measurements and the titration of sodium ion, it can be seen that a sodium ion links to two salicylaldehyde molecules, one of them being a molecular rest ion of salicylaldehyde and the other a salicylaldehyde molecule. The structures of these compounds will be illustrated in Fig. 1.

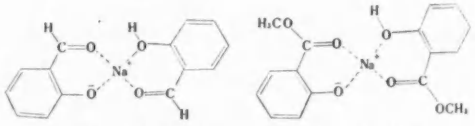


Fig. 1. The sodium compounds of salicylaldehyde and methylsalicylate.

The OH stretching vibrations of the sodium compounds show higher frequencies than those of salicylaldehyde and methylsalicylate. The broad band at 3100 cm^{-1} for salicylaldehyde changes into the sharp band at 3344 cm^{-1} for the sodium compound. The band at 3141 cm^{-1} for methylsalicylate separates into the two bands having their maxima at 3351 cm^{-1} and 3206 cm^{-1} for the sodium compound. The shifts of the OH stretching vibrations caused by changing salicylaldehyde and methylsalicylate into their sodium compounds indicate that the strong intramolecular hydrogen bond in the former varies into the intermolecular hydrogen bond in the latter. The two OH bands for the sodium compound of methylsalicylate may show the existence of the two different types of intermolecular hydrogen bond.

Concerning the sodium compounds, only one band can be assigned to the C=O stretching vibration for each compound. With the vibrations of metal chelate compounds, the couplings between ligand molecules are usually neglected. This approximation may be applied to these

sodium compounds because of the weakness of the metal-oxygen coordinate bonds. The same C=O stretching frequencies for salicylaldehyde and its molecular rest, coordinating to a sodium ion, suggest that the two carbonyl bonds are in the same electronic state. It is deduced that the lone pair electrons on the ionized oxygen in the molecular rest delocalize too little to influence the carbonyl group through the benzene ring. The fact that the carbonyl frequency of the C=O band for sodium compound of salicylaldehyde is higher than that for salicylaldehyde, may be explained by the small value of the electron affinity of sodium ion. As for the electron transfer of the oxygen atom in the carbonyl group, the larger the electron affinity of electron acceptors, the easier the electron transfer. The lone pair electrons on the oxygen atom, therefore, are less drawn by sodium ion than by proton and the frequency of the C=O band is higher for the sodium compound than for salicylaldehyde. The frequency of the C=O band for the sodium compound of methylsalicylate is slightly higher than that for methylsalicylate[10]. Since the coordinate bond between the sodium ion and the carbonyl group is very weak, the carbonyl group of the sodium compound of salicylaldehyde as well as that of *o*-methoxybenzaldehyde will be rather akin to that of virtual nonchelate salicylaldehyde. The difference in the C=O frequency between salicylaldehyde and its sodium compund is 17 cm^{-1}, while that between methylsalicylate and its sodium compound is only 3 cm^{-1}. This fact indicates the strong chelation in salicylaldehyde. This agrees with the results obtained by the solvent effect and the band shapes. The configuration of the sodium compound is probably of a tetrahedral type, since the available orbitals of sodium ion to form the coordinate bond are sp^3 hybrid. However, it has recently been reported[11] that the sodium compound of salicylaldehyde does not form any chelate ring because of the observed high frequency of the C=O band. Based on the present studies this opinion can be left out of consideration.

As regards chelate compounds, the bands assigned to the phenolic C–O stretching vibrations are of considerable interest, because no definite assignment for these bands has yet been made. By comparing the absorption spectrum of salicylaldehyde or methylsalicylate with that of its sodium compound respectively, the phenolic C–O bands are reasonably assigned. The results obtained are listed in Table VIII. The relations between wave numbers of C=O stretching and those of phenolic C–O stretching vibrations are given in Fig. 2.

TABLE VIII. THE WAVE NUMBERS OF C=O AND PHENOLIC C–O STRETCHING VIBRATIONS

	Salicylaldehyde		Methylsalicylate	
	C=O	C–O	C=O	C–O
Na^+	1680	1246	1682	1213
H	1663	1276	1679	1212
Ti^{4+}	1637	1313	1651	1246
Cu^{2+}	1612	1340		

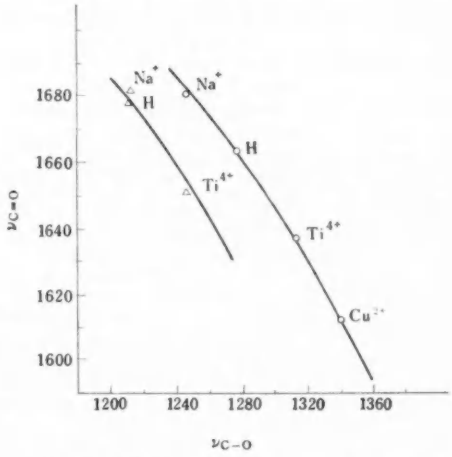


Fig. 2. The relations between the wave numbers of C=O stretching and those of phenolic C–O stretching vibrations. ○ Salicylaldehyde and its metal complexes. △ Methylsalicylate and its metal complexes.

In Table VIII and Fig. 2, copper complex and titanium complexes[12] are shown together. The larger the wave number of C=O stretching vibration, the smaller the wave number of C–O stretching vibration. The reason for this may be as follows. In these chelate compounds, as the double bond character of the C=O bond decreases by the electron migration from the carbon to the oxygen, the electron migration from the oxygen to the benzene ring and the

10) It is supposed that the C=O frequency of the sodium compound of methylsalicylate is hardly affected by the change in the nature of the C–O bond neighboring the C=O bond.

11) P. Chiorboli and P. Mirone, *Ann. chim.*, **48**, 363 (1958).

12) A. Yamamoto, to be published.

double bond character of the C–O bond increase. These relations are nearly linear and the curve for salicylaldehyde and its complexes and that for methylsalicylate and its complexes are parallel. From Fig. 2, it follows that the electron affinities of these electron acceptors are probably in the order of $Cu^{2+} > Ti^{4+} > H > Na^{+}$.

The author wishes to express her sincere thanks to Professor K. Kozima for his kind guidance and discussion throughout the course of this study and also to Mr. W. Suetaka for his helpful advice.

Research Laboratory of Spectroscopy
Tokyo Institute of Technology
Meguro-ku, Tokyo

Vinyl-polymerization with Alkylboron Derivatives

By Nobuyuki ASHIKARI

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The outline of alkylboron derivatives as the catalysts for the polymerization of vinyl compounds was previously reported[1]. In the present paper, the preparation of these catalysts, the polymerization rates, the relation between the conversion and the molecular weight, and the influence of oxygen on the polymerization rate are described in detail. The catalysts studied were dialkylboron chloride (R_2BCl), dialkylboronous ester (R_2BOR'), dialkylborinic acid (R_2BOH), and dialkylboron oxide [$(R_2B)_2O$]. Furukawa[2] reported that dialkylboron oxide was a good catalyst. The present investigation shows that the organoboron compounds employed in this experiment are effective for comparatively polar monomers.

Experimental and Results

Analytical Methods for Organoboron Compounds.—The synthesized catalysts were analyzed by the following methods. In the case of R_2BCl, hydrogen chloride produced by the decomposition of the sample with water was titrated with sodium hydroxide solution under phenolphthalein indicator. In other cases, quantitative analysis of boron was carried out by the modification of Synder's method[3].

A weighed sample (about 0.2 g.) was taken in a 100 cc. Erlenmeyer flask in which air was previously replaced with nitrogen. After 0.1 N sodium hydroxide solution, the amount of which was nearly equivalent to the theoretical value, was poured into the flask; 30% hydrogen peroxide solution was added slowly to it. The flask was shaken for twenty minutes. Then, the content was transferred into a platinum vessel to be heated gently. After the water was mostly vaporized, the vessel was cooled to room temperature, and the content was poured into a 300 cc. beaker with about 70 cc. of distilled water. To the aqueous solution about 5 cc. of glycerin was added and the titration was carried out with 0.1 N sodium hydroxide solution using phenolphthalein indicator. If the excess of alkaline solution is added at the beginning, the solution containing the sample has to be acidified by the addition of the known volume of hydrochloric acid (0.1 N) before the titration with sodium hydroxide solution is carried out.

The Monomers and the Treatments of the Polymers.—The monomers such as styrene (St), methyl methacrylate (MMA), and vinyl acetate (VA) were purified as mentioned below.

St: The "commercial" was washed with 5% alkaline solution, followed by water, dried over calcium chloride, and distilled.

VA: The "commercial" was steam distilled, dried over sodium sulfate, and distilled.

MMA: It was dried with sodium sulfate and distilled.

The distillation of styrene and methyl methacrylate was carried out under reduced pressure. The polymers except for polyvinyl acetate were treated with methanol, filtered, and dried. In the case of polyvinyl acetate, it was separated from its monomer by steam distillation.

Preparation of the Alkylboron Derivatives.—*Alkylboron chloride.*—The alkylboron chlorides were prepared according to Booth's method[4], i. e., by passing dry hydrogen chloride into trialkylboron. The reaction proceeds as follows:

$$R_3B + HCl = R_2BCl + RH$$

Using this method, diisopropylboron chloride,

1) N. Ashikari, *J. Polymer Sci.*, **28**, 641 (1958).
2) J. Furukawa, T. Tsuruta et al., *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **61**, 733 (1958).
3) H. R. Synder, J. A. Kuck and J. R. Johnson, *J. Am. Chem. Soc.*, **60**, 110 (1938).

diisobutylboron chloride and di-*n*-butylboron chloride were prepared.

To a 100 cc. round bottomed flask, were set an inlet of hydrogen chloride, and a condenser to the top of which a calcium tube was connected. Into this flask 36 g. of triisobutylboron was poured, and hydrogen chloride was introduced. The reaction was continued for 15 hr. at 140°C. Then, the content was distilled under reduced pressure, and the fraction of b. p. $_{31}62\sim65$°C was collected. Thus, 28 g. of diisobutylboron chloride was obtained (87% yield).

Analysis.—A weighing bottle containing 0.3116 g. of the sample was put in a 300 cc. flask containing 100 cc. of distilled water. The weighing bottle was tied with wire to the rubber stopper of the flask as shown in Fig. 1. After the rubber

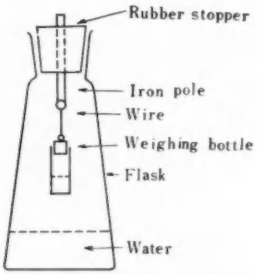


Fig. 1. The vessel for the decomposition of R_2BCl.

stopper was closed, the flask was shaken vigorously to open the stopper of the weighing bottle. The rubber stopper was taken off, and the titration was carried out. The amount of the spent sodium hydroxide solution (0.1 N) was 21.6 cc.

Anal. Found: Cl, 22.42. Calcd. for $(C_4H_9)_2BCl$: Cl, 22.12%.

Similarly, other dialkylboron chlorides were analyzed. The conditions of the preparation and the yields are shown in Table I.

TABLE I. ALKYLBORON CHLORIDE

R in R_2BCl	Temp. °C[a]	Time hr.	b. p. °C	Yield %
iso-C_3H_7	120	15	125	88
n-C_4H_9	140	15	67/18 mmHg[b]	82

a) Reaction temperature
b) Booth's value is 173°C[4].

Generally, dialkylboron chloride is rather more unstable to oxygen than the corresponding trialkylboron. For example, diisopropylboron chloride is inflammable in contact with air, but triisopropylboron is not so.

Dialkylboronous ester.—This is easily prepared by the reaction between dialkylboron chloride and alcohol[5]. The reaction formula is as follows:

$$R_2BCl + R'OH = R_2BOR' + HCl$$

Using this method various dialkylboronous esters were prepared. When alcohol was dropped slowly into dialkylboron chloride under nitrogen stream, the reaction took place at once.

The product consisted of two layers. The upper layer was colorless and the lower one, the amount of which was small, was slightly colored. The upper layer was separated from the lower one and distilled. Few studies on the esters of such type as $(iso\text{-}C_3H_7)_2BOR$ have been performed. The yields and the boiling points of these derivatives are shown in Table II.

TABLE II. THE YIELD AND THE BOILING POINT OF $(iso\text{-}C_3H_7)BOR$

R in $(iso\text{-}C_3H_7)_2BOR$	ROH (g.) added	Yield %	b. p. °C
CH_3	3	91.1	117
C_2H_5	4	80.0	132
iso-C_3H_7	5	80.7	51 (32 mmHg)
iso-C_4H_9	6	70.1	70 (32 mmHg)
tert-C_4H_9	6	35.5	92 (30 mmHg)

In Table II, the weigt of the diisopropylboron chloride used was 10 g. in each experiment. Moreover, diisobutylboron isobutyl ester was prepared. This boiled at 97°C/27 mmHg. The yield was 92%.

Analysis of $(iso\text{-}C_3H_7)_2BO(iso\text{-}C_3H_7)$
Sample: 0.1935 g., alkali added: 12.7 cc.
Found B, 7.25%, Calcd. B, 7.05%

Dialkylborinic acid and dialkylboron oxide.—Dialkylborinic acid was prepared according to Eq. 1, but was not always isolated purely because of decomposition by distillation.

$$R_2BCl + H_2O = R_2BOH + HCl \quad (1)$$

Dialkylboron oxide was prepared purely by distillation of the product from dialkylboron chloride and equivalent water. To 28.5 g. of di-*n*-butylboron chloride was added 3.2 g. of pure water under nitrogen stream, and the product was distilled. Thus, 18.5 g. of the product which boiled at 90~92°C/1 mmHg (reported value[6], 136°C/12 mmHg) was obtained (78.3% yield, calculated from di-*n*-butylboron chloride).

Analysis of $[(n\text{-}C_4H_9)_2B]_2O$
Sample: 0.1419 g., alkali added: 10.8 cc.
Found B, 8.41%, Calcd. B, 8.27%

The Rate of the Polymerization of Styrene with these Derivatives.—By observing the polymerization rates, the activities of these catalysts were compared. The catalysts employed in this experiment were isopropylboron derivatives. In

TABLE III. THE SORT AND WEIGHT OF THE CATALYST IN THE POLYMERIZATION OF STYRENE

Catalyst type	Weight, g.	Wt. of St, g.
R_2BOR	0.3681	130
R_2BCl	0.3562	148
$(R_2B)_2O$	0.4022	106

Where, R is iso-C_3H_7.

4) R. B. Booth and C. A. Craus, ibid., **74**, 1415 (1952).
5) M. F. Lappert, *Chem. Revs.*, **56**, 1015 (1956).
6) J. R. Johnson, H. R. Synder and M. G. Van Campen, Jr., *J. Am. Chem. Soc.*, **60**, 115 (1938).

TABLE IV. THE CONDITION OF THE POLYMERIZATION FOR INVESTIGATING THE RELATION BETWEEN THE CONVERSION AND THE INTRINSIC VISCOSITY

Monomer	Temp., °C	Vessel	Cat.[a]/monomer wt. %	O_2 mol. ($\times 10^5$)
MMA	50	flask	0.296	N_2 stream
St	50	flask	0.379	N_2 stream
VA	50	ampoule	0.414	5.0

a) The catalyst is diisopropylboron oxide.

every case, the value of catalyst/monomer was 0.188 in mol. %. The weights of the catalysts and the monomer were shown in Table III.

Each reaction was carried out at 50°C under nitrogen stream in a four necked flask to which a stirrer, an inlet of nitrogen, and a thermometer were connected.

At a certain interval of reaction, 10 g. portions of the sample were taken out and poured into methanol. Then, the polymer was filtered, dried, and weighed. These results were represented in Fig. 2.

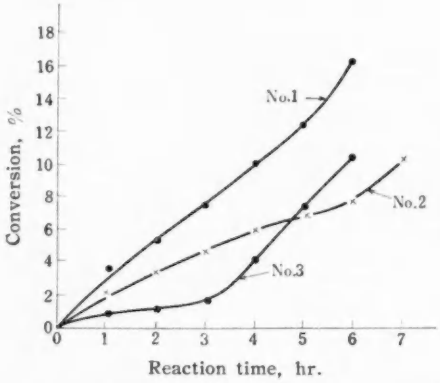


Fig. 2. Polymerization rates of styrene with three types of alkylboron.
No. 1, $(R_2B)_2O$: No. 2, R_2BOR: No. 3, R_2BCl, where, R is iso-C_3H_7.

Usually, in the polymerization with these catalysts, the polymerization rate increased rapidly after a certain reaction time (as shown in Fig. 2).

Relation between the Conversion and the Molecular Weight.—In usual "radical polymerization", the molecular weight is expected to have no relation with the conversion. However, in high conversion, many examples[7] have shown the fact that the former depends on the latter. The same phenomenon was observed, even in low conversion, in the case of the polymerization with alkylboron catalyst. Methyl methacrylate, styrene and vinyl acetate were polymerized in the following conditions (Table IV).

When the reaction was carried out in an ampoule, the apparatus shown in Fig. 4 was used. When a flask was used as a reaction vessel, the reaction was carried out under nitrogen stream, and the sample was taken out after a certain interval of reaction. The relation between the conversion and the intrinsic viscosity was represented in Fig. 3.

In this case, the viscosity of each polymer was measured in the following condition (Table V).

TABLE V. THE CONDITION OF MEASUREMENT OF THE VISCOSITY

Polymer	Solvent	Temp., °C
PMMA	toluene	30
PSt	toluene	30
PVA	benzene	30

Where, "P" means a polymer.

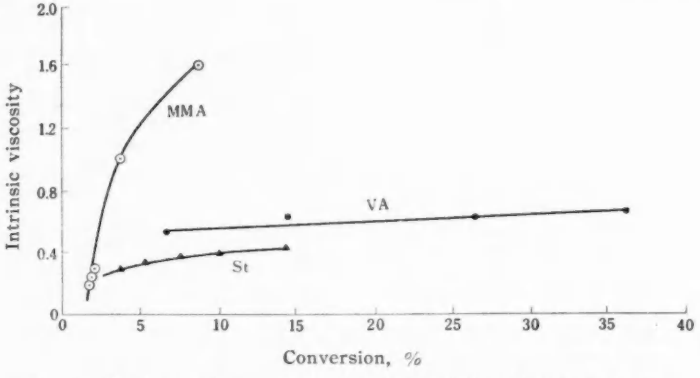


Fig. 3. Relation between the conversion and the intrinsic viscosity.

7) M. Ōiwa, *Chemistry and Chem. Ind.* (*Kagaku to Kogyo*), **11**, 792 (1958).

TABLE VI. POLYMERIZATION CONDITIONS FOR INVESTIGATING THE INFLUENCE OF OXYGEN

Monomer	Time, hr.	Temp., °C	Catalyst	Catalyst/monomer, wt. %	Cat., wt.
St	5	40	R_2BO·iso-C_3H_7	0.42	0.0754
MMA	1	40	R_2BO·iso-C_3H_7	0.40	0.0754
VA	0.5	41	R_2BO·iso-C_4H_9	0.41	0.0766

Where, R is iso-C_3H_7.

TABLE VII. MEASUREMENT OF THE VISCOSITIES AND THE EQUATIONS FOR CALCULATING THE MOLECULAR WEIGHT

Polymer	Solvent	Temp., °C	Eq. ($[\eta]=$)	Reference
PSt	toluene	30	$0.55\times10^{-4}M^{0.81}$	8
PMMA	toluene	25	$0.71\times10^{-4}M^{0.73}$	9
PVA	benzene	30	$5.63\times10^{-4}M^{0.62}$	10

Influence of Oxygen on the Polymerization Rate.—To observe the influence of oxygen on the polymerization rate some monomers were polymerized in the following apparatus (Fig. 4).

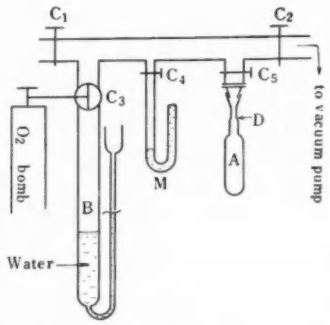


Fig. 4. Apparatus for investigating the influence of oxygen.
M: Manometer
B: Gas burette
A: Polymerization tube

The Explanation of the Apparatus and the Procedure.—The volume of the space enclosed by stopcocks C_1–C_5 is 136 cc., and that of A, polymerization tube, is 70 cc. The volume from C_5 to D is 5 cc.

To tube A in which nitrogen had replaced air, 20 cc. of monomer was introduced and the tube was cooled in dry-ice methanol. After the catalyst, the amount of which was shown in Table VI, was added under a nitrogen stream, the tube was connected to the apparatus. The gas involved in tube A and other spaces enclosed by stopcocks C_1–C_4 was removed by a vacuum pump. After a certain amount of oxygen contained in burette B was introduced to the tube, it was sealed. The sealed tube was transferred into a constant temperature bath. The reaction temperature, the reaction time, etc., were shown in Table VI.

Thus, from the yield obtained after the same reaction time, the influence of oxygen on the polymerization rate was compared. The relation between the amount of oxygen and the conversion was represented in Fig. 5.

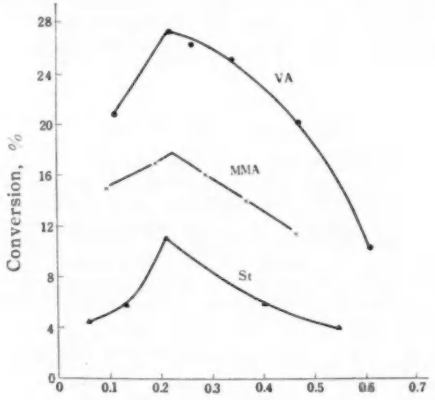


Fig. 5. Diagram of conversion—O_2/catalyst. The influence of oxygen on the polymerization rate.

The viscosity of each sample shown in Fig. 5 was measured to obtain the relation between the molecular weight and the value of O_2/catalyst in mole ratio. These results are represented in Fig. 6. The conditions of measurement of the viscosity and the equations for calculation of the molecular weight are shown in Table VII.

From Fig. 5, it is clear that the polymerization rate is the largest when the value of O_2/catalyst in mole ratio is 0.22. In regard to the molecular weight, the molecular weight at the maximum point of the polymerization rate is minimum except in the case of polyvinyl acetate. The reason why the curve of the molecular weight of PVA against the mole ratio of O_2/catalyst differed from those of polymethyl methacrylate and polystyrene is not clear.

8) T. Alfrey and Batovics, *J. Am. Chem. Soc.*, **65**, 2319 (1943).
9) S. Chinai, J. Matlack and A. Resnick, *J. Polymer Sci.*, **17**, 391 (1955).
10) A. Nakajima, *Chemistry of High Polymers (Kobunshi Kagaku)*, **11**, 142 (1954).

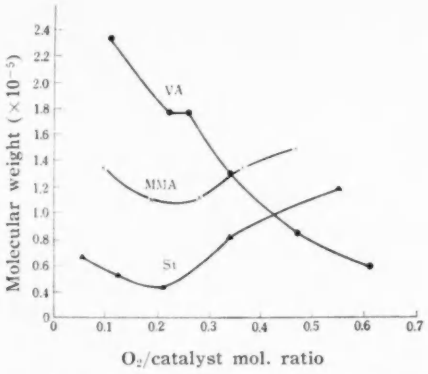


Fig. 6. Relation between the molecular weight and O_2/catalyst mol.-ratio.

Summary

Such alkylboron derivatives as dialkylboron chloride, dialkylborinic acid, dialkylboronous ester, and dialkylboron oxide as the catalysts for the polymerization of vinyl compounds were studied. Although dialkylborinic acid was a good catalyst, it was pretty difficult to isolate it purely, therefore, only a brief description was made in this paper. Of course, some dialkylborinic acids can be isolated purely under suitable conditions. In regard to this, further investigation will be performed.

The polymerization rates of styrene with these catalysts, the relation between the conversion and the intrinsic viscosity, and the influence of oxygen on the polymerization rate were studied. The polymerization rate of some monomers with dialkylboronous ester is maximum when O_2/catalyst in mole ratio is 0.22.

The author wishes to express his sincere thanks to Mr. T. Iwachido in this laboratory who measured the viscosities.

The Electrical Communication Laboratory
Nippon Telegraph and Telephone
Public Corporation
Musashino-shi, Tokyo

Polymerization of Olefins with Trialkylboron Catalyst. III. Copolymerization of Butadiene, Isobutylene and 1-Phenylbutadiene

By Nobuyuki ASHIKARI

(Received April 15, 1959)

As is well known, the monomers having comparatively large polarity easily polymerize with alkylboron catalyst, but those having small polarity do not. The polymerizations of the monomers which polymerize alone, and the copolymerizations of those monomers have already been reported[1,2]. In this paper, the copolymerizations of some monomers which exhibit no tendency to polymerize alone, such as butadiene, isobutylene, and 1-phenylbutadiene were studied. In every pair of the monomers treated in this paper, the copolymerization rates were very small. Particularly, the reaction rate of 1-phenylbutadiene with another monomer was so small that the relative reactivity could not be obtained. The relative reactivities of such pairs as isobutylene-acrylonitrile, butadiene-styrene and butadiene-acrylonitrile were obtained.

Experimental and Results

1. Monomers.—*1) Isobutylene and butadiene.*—Isobutylene[3] was prepared by dehydration of *tert*-butanol with anhydrous oxalic acid at about 90°C, dried over calcium chloride, and redistilled. Butadiene was prepared according to Blatt's method[4], i.e., thermal decomposition of cyclohexene, dried over calcium chloride, and redistilled.

2) Acrylonitrile, styrene and methyl methacrylate.—The commercial substances were dried and distilled just before use.

3) 1-Phenylbutadiene.—This was synthesized

1) N. Ashikari, This Bulletin, **31**, 229 (1958).
2) N. Ashikari, *J. Polymer Sci.*, **31**, 249 (1958).
3) N. Daidan et al., *J. Electrochem. Soc. Japan (Denki Kagaku)*, **13**, 27 (1945).
4) A. H. Blatt et al., "Organic Syntheses", Col. Vol. II, John Wiley & Sons, Inc., New York (1943) p. 655.

from cinnamic aldehyde by the following method[5,6]:

$$\underset{(A)}{RCHO} \xrightarrow{CH_3MgJ} \underset{(B)}{RCH(OMgJ)CH_3} \xrightarrow{NH_4Cl\text{-}H_2O} \underset{(C)}{RCH(OH)CH_3}$$

$$\xrightarrow{HCl} \underset{(D)}{RCHClCH_3} \xrightarrow{-HCl} \underset{(E)}{RCH=CH_2}$$

Where, R is $C_6H_5CH=CH-$.

D was prepared by treating C with dry hydrogen chloride at 0°C, and E was prepared by heating D in pyridin solvent for about one hour. After the reaction was over, unchanged pyridin was distilled off, and the product was washed thoroughly with water to remove the complex of pyridin-hydrogen chloride. Then, the product was dried over calcium chloride and distilled. The yield of pure 1-phenylbutadiene boiling at 56~57°C/3 mmHg was 17~20% of the theoretical amount for cinnamic aldehyde.

II. Procedure of the Copolymerization and the Treatment of the Polymer.— In a polymerization tube, a certain amount of high-boiling monomer such as styrene or acrylonitrile was placed, and the tube was cooled in dry ice-methanol. After the content was thoroughly cooled, the tube was placed on a balance, and a certain amount of second monomer, liquefied by cooling, such as isobutylene or butadiene was poured into the tube. Then, the catalyst, triisobutylboron was added to the tube under nitrogen stream, and the tube was sealed.

The reaction was stopped by cooling the tube in dry ice-methanol. After the tube was opened, the polymer was precipitated by adding the content of the tube into methanol, filtered, dried under reduced pressure at 50°C, and weighed. If the copolymerization was carried out in emulsion system, the polymer was taken out by treating the content with hot water (about 90°C) containing 5% sodium chloride. Thus, the polymer isolated was washed thoroughly with hot water, followed with methanol, dried and weighed.

III. Copolymerization Rates of Butadiene-acrylonitrile in the Bulk and Emulsion Systems.—The copolymerization rate of butadiene-acrylonitrile in emulsion system was compared with that in bulk system.

Generally, the polymerization rate in emulsion system is larger than that in bulk system. In this experiment, the same results were obtained. Moreover, in emulsion system, fairly strong copolymer was obtained.

The total weight of the two monomers in each pair was 11.3 g., and the volume of the catalyst was 0.1 cc. in each experiment. In emulsion system, 12 cc. of distilled water containing 5% emulsifier was used. Each reaction was carried out in a sealed tube at 40°C for five hours. The relation between the conversion and the mole fraction of butadiene in the monomer mixture is shown in Fig. 1.

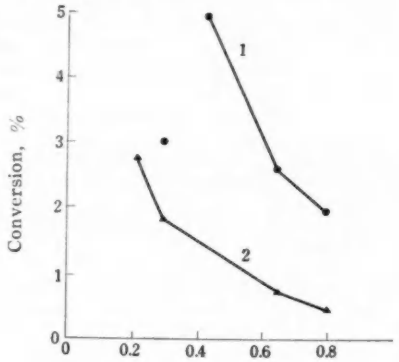


Fig. 1. Copolymerization rates of butadiene-styrene in bulk and emulsion system.
(1) emulsion system
(2) bulk system

IV. Monomer Reactivity Ratios.—The relative reactivities (r_1, r_2) of such pairs as isobutylene-acrylonitrile, butadiene-styrene, and butadiene-acrylonitrile were evaluated graphically using the following equation[7]:

$$r_2 = \frac{\log([M_2]_0/[M_2]) - \frac{1}{p}\log\frac{1-p[M_1]/[M_2]}{1-p[M_1]_0/[M_2]_0}}{\log([M_1]_0/[M_1]) + \log\frac{1-p[M_1]/[M_2]}{1-p[M_1]_0/[M_{02}]}}$$

where $p=(1-r_1)/(1-r_2)$, $[M]_0$ and $[M]$ represent the monomer concentration in the intitial and final states of polymerization, respectively,

TABLE I. ISOBUTYLENE-ACRYLONITRILE

No.	$[M_1]_0$	$[M_2]_0$	Conversion	N%	$[M_1]$	$[M_2]$
1	0.179	0.02	3.44	13.8	0.1757	0.0163
2	0.166	0.04	3.72	14.6	0.1626	0.0356
3	0.179	0.06	3.96	15.2	0.1750	0.0543
4	0.125	0.08	4.77	17.6	0.1218	0.0733
5	0.100	0.10	5.53	18.0	0.0966	0.0923
6	0.116	0.12	5.54	18.7	0.1123	0.1105
7	0.061	0.14	9.02	21.1	0.0575	0.1253
8	0.054	0.18	8.26	21.9	0.0509	0.1638

5) E. C. Coyner and G. A. Ropp, *J. Am. Chem. Soc.*, **69**, 2231 (1947).
6) A. Klages, *Ber.*, **35**, 2650 (1902).
7) F. R. Mayo and C. Walling, *Chem. Revs.*, **46**, 207 (1950).

TABLE II. BUTADIENE-ACRYLONITRILE

No.	$[M_1]_0$	$[M_2]_0$	Conversion	N%	$[M_1]$	$[M_2]$
1	0.0500	0.4490	4.45	15.46	0.04094	0.43599
2	0.1000	0.4000	3.81	13.57	0.09088	0.39019
3	0.0759	0.1755	3.82	12.73	0.07101	0.17084
4	0.1000	0.1509	0.64	11.98	0.09914	0.15017
5	0.2000	0.2000	2.26	11.18	0.19484	0.19614
6	0.2000	0.0509	1.78	8.06	0.19691	0.04951

TABLE III. BUTADIENE-STYRENE

No.	$[M_1]_0$	$[M_2]_0$	Conversion	C%	$[M_1]$	$[M_2]$
1	0.0315	0.200	4.28	90.96	0.02447	0.19439
2	0.0472	0.175	2.99	91.14	0.04512	0.17107
3	0.0631	0.150	2.32	90.78	0.05925	0.14770
4	0.1000	0.100	1.45	89.04	0.09607	0.09983
5	0.0944	0.100	2.01	89.68	0.08996	0.09931
6	0.2202	0.150	1.34	89.20	0.21399	0.14968

and subscripts 1 and 2 mean that the corresponding quantities are concerned with components 1 and 2, respectively.

The values of $[M_1]$, $[M_2]$, conversion, etc., are shown in Tables I—III.

The relative reactivities (r_1, r_2) are shown in Table IV. Table V shows the values in the case of radical type determined by other investigators[8].

TABLE IV. RELATIVE REACTIVITIES

	iB-AN	Bd-AN	Bd-St
r_1	0.02±0.02	0.40±0.02	1.30±0.1
r_2	1.8 ±0.2	0.04±0.01	0.01±0.01
T	50	50	43

iB: isobutylene, AN: acrylonitrile,
Bd: butadiene, T: reaction temp. (°C)

TABLE V. THE VALUES OF (r_1, r_2) REPORTED ON EARLIER PAPER

	Bd-AN	Bd-St
r_1	0.35±0.01	1.48±0.08
r_2	0.05±0.01	0.23±0.07
T	50	50

V. Infrared Spectra and Turbidity Measurement of 1-Phenylbutadiene—Methyl Methacrylate Copolymer.—It had not been clear whether 1-phenylbutadiene enters into a copolymerization reaction or not. In this respect, the copolymerization of this monomer with methyl methacrylate was carried out to make this point clear. As previously mentioned, 1-phenylbutadiene does not polymerize alone with organo boron catalyst, but does thermally. Therefore, even if the two components are present in the product, it does not always mean a copolymer. For the purpose of looking over the product, infrared spectra and turbidity measurement of the product were employed.

V-1) Copolymerization of 1-phenylbutadiene with methyl methacrylate.—The monomer mixture (feed 1 : 1) consisted of 1-phenylbutadiene and methyl methacrylate (0.0237 mol.) was polymerized with 0.1 cc. of triisobutylboron catalyst in a sealed tube at 50°C for 15 hr. The product precipitated with methanol was redissolved in benzene and precipitated with methanol two times. Thus, 0.0702 g. of the polymer was obtained (conversion: 1.3%).

V-2) Infrared spectra.—The infrared spectrum of the sample obtained above was observed in

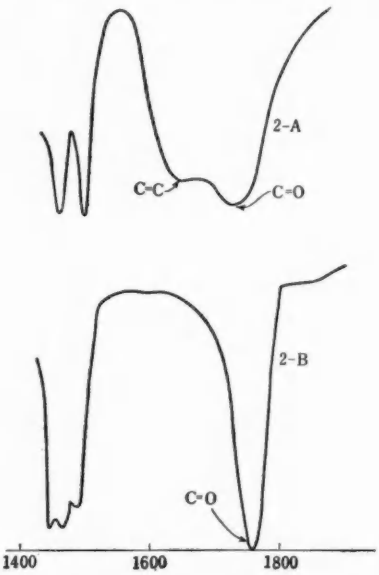


Fig. 2. Infrared spectra of phenylbutadiene-methyl methacrylate copolymer and polymethyl methacrylate.
A, 1-Phenylbutadiene—methyl methacrylate copolymer
B, Polymethyl methacrylate

8) T. Alfrey, J. J. Bohrer and H. Mark, "High Polymers", Vol. VIII, "Copolymerization" Interscience Publishers, Inc., New York (1952), p. 32, 44.

order to confirm the presence of the two components. Fig. 2-A is the spectrum of the sample, and Fig. 2-B is that of polymethyl methacrylate prepared with alkylboron catalyst.

Comparing A with B, it is clear that the product obtained in paragraph V-1 is not identical with polymethyl methacrylate. In Fig. 2-A, the absorption band at about 1650 cm^{-1} owes to C=C, and the band at about 1740 cm^{-1} owes to C=O of methyl methacrylate. Of course, the absorption band of C=C indicates the existence of poly-(1-phenylbutadiene) shown below.

poly(1-phenylbutadiene): $[-CH-CH=CH-CH_2-]_n$
C_6H_5

V-3) Measurement of turbidity. — The sample obtained in paragraph V-1 was dissolved in 200 cc. of acetone and the turbidity was measured utilizing a nephelo-titrator. The same measurements were carried out with thermally polymerized 1-phenylbutadiene and polymethyl methacrylate prepared with alkylboron catalyst.

In every case, the condition of the measurement was as follows: solvent, acetone; nonsolvent, distilled water; concentration, 0.0070%; temperature, 25°C. These results are represented in Fig. 3.

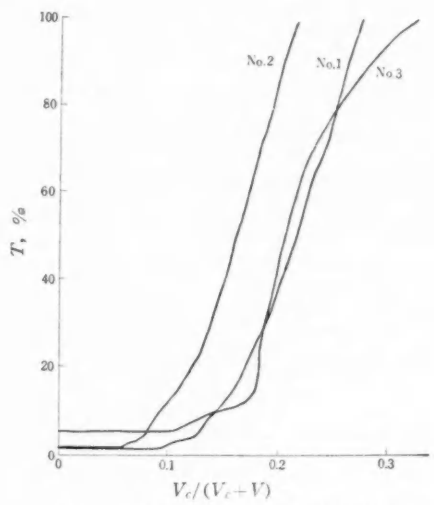


Fig. 3. Diagram of $T-V_c/(V_c+V)$.
T: turbidity, V_c: volume of water,
V: volume of acetone.
No. 1, Copolymer
No. 2, Phenylbutadiene
No. 3, Methyl methacrylate

Comparing No. 1 with No. 2 and 3 in Fig. 3, it may be considered that 1-phenylbutadiene copolymerizes with methyl methacrylate.

Discussion

Diagram of $T-V_c/(V_c+V)$.—If the product (1-phenylbutadiene-methyl methacrylate) is a mixture of the two components, the influence of 1-phenylbutadiene must be more striking around the bottom of No. 1 in Fig. 3. Moreover, the product is a low polymer, so that when it contains the greater part of polymethyl methacrylate, the bottom of No. 1 must be situated on the right side of No. 3. From the viewpoint mentioned above, the product obtained in paragraph V-1 may be considered as a copolymer.

The Relative Reactivities.—The following methods have been employed for obtaining the composition in a copolymer which consists of C and H atoms:

a) from analytical value of C atoms,
b) from refractive index,
c) from ultraviolet absorption.

Any method will contain more or less errors. In this respect, a) is, particularly, apt to contain an error.

Therefore, some questions will be present in the relative reactivity in the copolymerization of butadiene-styrene, reported in this paper. In this respect, the other methods will be employed to the butadiene-styrene copolymer.

As is well known, the mechanism of the polymerization with alkylboron catalyst is a radical type. The propriety of the mechanism is proved in this paper also, comparing the values of the relative reactivities obtained in this experiment with those in the copolymerization with peroxide catalyst.

Summary

The relative reactivities in the copolymerization of some monomers which do not polymerize alone with alkylboron catalyst, with those which polymerize alone, were obtained. The copolymerization rate of 1-phenylbutadiene with another monomer was so small that the relative reactivity could not be obtained. But, from the studies on the reaction product of 1-phenylbutadiene and methyl methacrylate, it was considered that the former copolymerized with the latter.

The author wishes to express his sincere thanks to Messrs. K. Abe and K. Yanagisawa in this laboratory for their kindness observing the infrared spectra.

The Electrical Communication Laboratory
Nippon Telegraph and Telephone
Public Corporation
Musashino-shi, Tokyo

Analytical Chemistry by Means of Organic Compounds. XXV[1]. *1-Hydroxyacridine as a New Reagent (Neo-oxine) (1)*

By Masayoshi ISHIBASHI, Yuroku YAMAMOTO and Hirohiko YAMADA

(Received February 13, 1959)

It is expected that 1-hydroxyacridine will be useful in analytical chemistry, because it has the same functional group as 8-hydroxyquinoline (oxine) which is one of the most valuable organic reagents in various fields such gravimetry, volumetry, or colorimetry. Irving et al.[2] have investigated the behavior of this compound to some metallic ions such as aluminum, chromium, iron(III), gallium, copper and zinc, concerning the study for the effects of steric hindrance of some oxine derivatives. It was found by them that 1-hydroxyacridine and 2-methyl-oxine did not form precipitate with aluminum, while forming precipitate with other metals, and the reason of the failure of these reagents to react with aluminum was attributed to steric hindrance of the groups in the 2-position of oxine. In the presence of aluminum, 2-methyl-oxine was used by Merrit[3] as a precipitant for zinc, or by Motojima[4] as not only a precipitant but also a coloring reagent for beryllium and titanium.

There is, however, no reference for use of 1-hydroxyacridine in analytical chemistry. It is presumed that this compound is more favorable in gravimetry or colorimetry with solvent extraction because of larger molecular weight than that of oxine or its derivatives. Moreover, this compound has the feature of not reacting to aluminum ion and this selective behavior will be advantageously used in determining some metals in the presence of aluminum without preliminary separation.

It is the purpose of this study to investigate the reaction between 1-hyroxyacridine and numerous cations which are used to be reactive with oxine, and to apply the results for gravimetry or colorimetry with solvent extraction.

The present paper is concerned with the results obtained by spectrophotometric method with solvent extraction. Absorption spectra were taken for the reagent in acidic, neutral and alkaline medium. Both acidic and basic ionization constants were then obtained, according to Stenstrom's method[5]. The basis for solvent extraction with chloroform were investigated for the chelate compounds of the reagent with some metals such as copper, cobalt, nickel and zinc. Reactions with other metals and another aspects of the study, such as formula, solubility and thermal stability of the chelate are under investigation and the results will be reported in the near future.

We propose to name this reagent as "neo-oxine".

Experimental and Results

Apparatus.—Spectrophotometric measurements were made with a Beckman quartz spectrophotometer, Model DU, with 1 cm. silica transmission cells having a tight stopper. A Beckman pH meter with glass electrode, Model H-2, was used for all pH measurements.

Materials.—*1-Hydroxyacridine.*—This compound was synthesized by the method described by Irving and his coworkers[2]. The crude product was recrystallized several times from 75% alcohol and dried in vacuo. The melting point of the dried sample was 115~116°C, identical with that in the literature.

Anal. Found: H, 4.82; C, 79.74; N, 7.17; O, 8.36. Calcd. for $C_{13}H_9ON$, H, 4.64; C, 79.99; N, 7.18; O, 8.22%.

The pure substance obtained is brownish yellow needles and slightly soluble in water but easily soluble in organic solvent such as alcohol, or chloroform. The solution of 1-hydroxyacridine was prepared to concentration of 10^{-3} M with 95% alcohol.

Chloroform.—It was purified by distillation.

Buffer solution.—Borate, phosphate and acetate buffers were prepared using each pure acid. To 1/25 M of each acid solution proper amounts of dilute sodium hydroxide solution were added to obtain the desired pH.

1) Paper XXIV of this series: M. Ishibashi and Y. Yamamoto, *Bulletin of the Institute for Chemical Research, Kyoto University*, **31**, 280 (1953).
2) H. Irving, E. J. Butler and M. F. Ring, *J. Chem. Soc.*, **1949**, 1489.
3) L. L. Meritt, *Record. Chem. Progr. (Kresge-Hooker Sci. Lib.)* **10**, 59 (1949).
4) K. Motojima, This Bulletin **29**, 29, 71, 458 (1956).
5) W. Stenstrom and N. Goldsmith, *J. Phys. Chem.*, **30**, 1683 (1926).

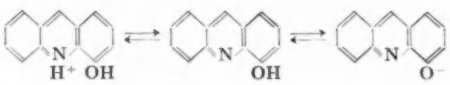
Metal solution.—All of the stock solutions of metals were prepared to concentration of 10^{-3} M. Cupric sulfate which was recrystallized from water and dried in room temperature, was dissolved and then diluted to the desired concentration. Cobaltous sulfate (Merk) was dissolved in water to approximately 10^{-1} M and after the concentration of the metal was checked by electrolysis, the solution was diluted to the desired concentration. Nickel solution was obtained by dissolving pure nickel ammonium sulfate. In the case of zinc the pure metal was dissolved in small amounts of nitric acid and after sulfuric acid was added, the solution was evaporated almost to dryness, and then diluted with water.

All other reagents as ethylenediamine tetraacetic acid, tartaric acid, cuproine (biquinolyl), dimethylglyoxime, etc., were analytical grade ones.

In the preliminary experiments, it was observed that ions such as copper, zinc, nickel, cobalt, iron, etc., were precipitated in slightly acidic (pH 5.1) or in a weak basic (pH 9.5) medium by 1-hydroxyacridine, forming red or reddish orange chelate compounds. It was also confirmed that the compound did not form a precipitate with aluminum in any medium. The filtrate which is obtained by filtrating the precipitate formed in slight excess of reagent, did not react to oxine, and it is presumed that the solubility of the metal chelate of 1-hydroxyacridine may be smaller than that of oxine chelate.

Absorption Spectrum of 1-Hydroxyacridine.—All of the solutions for absorbance measurements were prepared by diluting the required quantity of the stock solution using a buffer solution. The absorbance was measured in the range of 210~450 mμ against the respective buffer solution. Spectra obtained in acidic, neutral and alkaline mediums are shown in Fig. 1.

It is observed that many absorption bands exist in the ultraviolet region, and that the bands in neutral solution shift to longer wavelength with both the decreasing and increasing of pH. The change in absorption spectra with pH may be attributed to structural changes which are due to dissociation of 1-hydroxyacridine as follows, being similar to that of oxine.



Ionization Constant.—To evaluate basic and acidic ionization constants of the reagent, absorbance was then measured for twenty-six solutions having various pH's. In almost all cases, the pH was adjusted using respective buffer solution, but dilute sodium hydroxide or hydrochloric acid solution was used when stronger alkaline or acidic medium was necessary. The absorbance values at four different wavelengths were plotted against pH, as shown in Fig. 2. The phenolic or basic ionization constant was obtained as

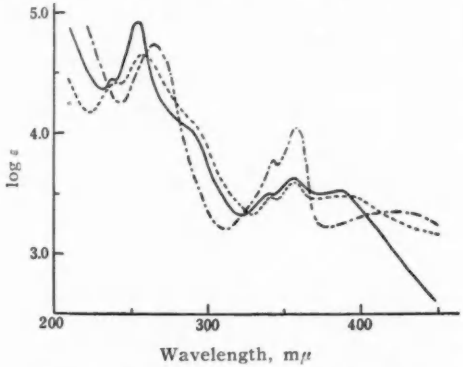


Fig. 1. Absorption spectrum of 1-hydroxyacridine.
—·—· pH 4.6, —— pH 7.2, ------ pH 9.5

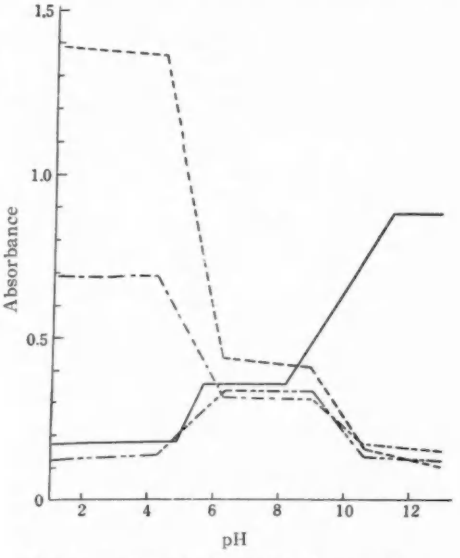


Fig. 2. pK_a and pK_b of 1-hydroxyacridine.
—— at 300 mμ, —·—· 343 mμ, ------ 359 mμ, ——·—— 380 mμ

TABLE I. IONIZATION CONSTANT OF 1-HYDROXYACRIDINE

Wavelength (mμ)	pK_a	pK_b
300	9.85	5.27
343	9.83	5.30
359	9.83	5.31
380	9.86	5.34
Mean	9.84	5.31

pK by a graphical determination of the pH at which the absorbance was half-way between its values in neutral and alkaline or acidic solution. According to Stenstrom and Goldsmith[5], the midpoint pH = pK_a or pK_b. The values obtained are listed in Table I. The pK_a and pK_b of oxine has been reported as 9.70 and 9.08 respectively by Phillips[6]. The pK_a of 1-hydroxyacridine is thus slightly greater than that of oxine, while pK_b is considerably smaller.

Absorption Spectra of 1-Hydroxyacridine and its Chelate in Chloroform. — Procedure of extraction is conducted as follows.

Each 2 ml. of reagent and metal solution (both 10^{-3} M) was pipetted into a separatory funnel having the mark of 20 ml., in which had been contained approximately 15 ml. of the buffer solution having the desired pH and was then diluted to the mark with water. Red or reddish orange precipitate was immediately formed by mixing. After standing for 20 min. or more to digest the precipitate, 10.0 ml. of freshly distilled chloroform was added, and the vessel was vigorously shaken for 2 min. or more. The extraction seemed to be complete, when the lower chloroform layer colored, but the aqueous layer became completely colorless. The organic extract was then transferred into a little Erlenmayer flask containing about 1 g. of anhydrous sodium sulfate. Absorbance was measured for the dried chloroform solution over a range of 300~600 mμ using chloroform as a reference solvent. The pH was measured for the aqueous phase which remained after extraction. Spectra are shown in Fig. 3, and the wavelength of maximum absorption is also listed in Table II. Quite similar experiments were made for the reagent solution, and the results are also shown in Fig. 3 and Table II. In the following experiments, all the extraction procedures are followed as above, unless otherwise indicated. It is seen that a specific absorption band for each chelate appears in the visible region at which the reagent does not show appreciable absorbance.

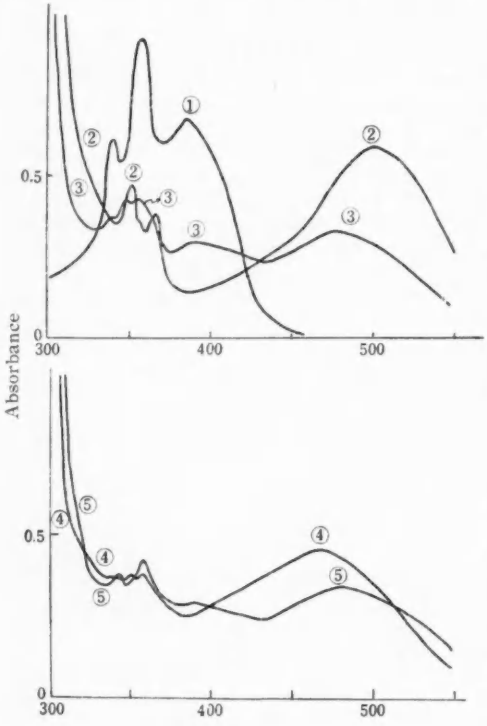


Fig. 3. Absorption spectra in chloroform.
① 1-Hydroxyacridine (extracted from pH 4.6)
② Copper chelate (〃 8.7)
③ Zinc chelate (〃 11.7)
④ Nickel chelate (〃 9.1)
⑤ Cobalt chelate (〃 11.7)

TABLE II. WAVELENGTH OF MAXIMUM IN CHLOROFORM (mμ)

1-Hydroxyacridine	341	358	386	
Copper chelate	353	358	368	502
Cobalt chelate	341	358	388	480
Nickel chelate	340	350	357	468
Zinc chelate	341	350	358 389	478

Effect of pH on Extraction.—To obtain optimum range of pH for the extraction of each element and reagent, the absorbance was measured for the organic extract from aqueous solution, the pH values of which had been adjusted to various values with respective buffer. The pH measurements were made for the aqueous phase after extraction and the absorbance was measured at wavelength of the respective peak of the metal chelate.

The results are shown in Fig. 4. The pH range of optimum extraction for the four metals is somewhat narrow, as compared with the metal chelate of oxine reported by several workers[9], contrary to the expectation. In order to obtain higher selectivity in a solvent extraction using chelate reagents, various masking reagents are extensively used. The effects of some complexing agents as cyanide, ethylenediaminetetraacetic acid and tartaric acid

6) J. P. Phillips and L. L. Meritt, *J. Am. Chem. Soc.*, **70**, 410 (1948).

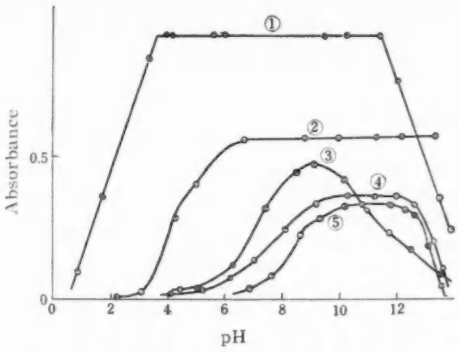


Fig. 4. Effect of pH on extraction.
① 1-Hydroxyacridine
② Copper chelate
③ Nickel chelate
④ Cobalt chelate
⑤ Zinc chelate

were thus investigated. It was found that these complexing agents inhibit the reaction of all metals with 1-hydroxyacridine. When a complexing agent is present in the concentration of 10^{-1} M, the precipitate does not form and the organic extract also does not show appreciable absorbance in the visible region.

Stability of the Metal Chelates.—The effects of time of standing were investigated for the organic extracts of the metal chelates. Standing the dried extract in the transmission cell with a stopper, the absorbance was measured at several intervals. Results are shown in Table III. The result is that the absorbance decreases slightly during the initial several minutes and then remains almost constant during 60~180 min. But when the solution was kept for 1 day, the absorbance had considerably decreased.

TABLE III. EFFECT OF STANDING TO ABSORBANCE

Time min.	Copper 502 mμ	Nickel 468 mμ	Cobalt 480 mμ	Zinc 478 mμ
0	0.554	0.448	0.330	0.305
1	.554	.447	.329	.303
2	.553	.445	.328	.303
3	.553	.443	.327	.303
5	.553	.442	.327	.302
10	.551	.439	.325	.302
20	.551	.438	.324	.300
30	.550	.437	.322	.299
60	.546	.433	.319	.299
90	.545	.433	.319	.299
120	.545	.433	.319	.299
180	.545	.433	.319	.299
1 day	.280	.231	.140	.102

Per Cent Extracted.—The per cent extracted at optimum pH in Fig. 4 was determined for the four elements. For zinc and cobalt, radioactive isotope was used as tracer, and for the other two, the amount of metal ion in aqueous or organic layer was determined by spectrophotometric method using sensitive organic reagents. The procedures are as follows and the results are listed in Table IV.

TABLE IV. PER CENT EXTRACTED

Element	%	pH
Copper	99.71	8.7
Cobalt	99.19	11.7
Nickel	99.10	9.1
Zinc	99.93	11.7

Copper.—Ten milliliters of cupric solution (10^{-3} M) and 5 ml. of the reagent solution (10^{-2} M) were pipetted into a 100 ml. volumetric flask. The solution was then diluted to the mark with the buffer solution. After standing, the red precipitate was extracted with 50 ml. of freshly distilled chloroform. The remaining aqueous solution was then evaporated to about 5 ml. on a sand bath. After cooling, the pH was readjusted to 5.5 with hydrochloric acid and about 1 g. of hydroxylamine hydrochloride was added in order to reduce cupric ion to cuprous. The cuprous ion was then extracted with 10.0 ml. of amyl alcohol containg 0.01% of cuproine[7]. The absorbance was measured at 540 mμ for the reddish violet organic extract. For the standard cupric solution (10^{-5} M), the same extraction procedure with amyl alcohol containing cuproine was done after reduction, and the absorbance was obtained similarly. The per cent of extraction was calculated from the two absorbance values.

Nickel.—The extraction was done under the same condition, except pH, as described above. The organic extract was destroyed by adding proper amount of concentrated perchloric acid and heating to fumes. After destroying organic matter completely, the solution was evaporated to dryness. The residue was dissolved and diluted with water and the amount of nickel ion was determined by dimethylglyoxime following the method described by Sandell[8].

7) J. Hoste and J. Gillis, *Anal. Chim. Acta*, **9**, 263 (1953).
8) E. B. Sandell, "Colorimetric Determination of Traces of Metals", Interscience Publishers, New York (1950), p. 470.

Cobalt.—Two milliliters cobalt (10^{-3} M), 1.0 ml. of the reagent (10^{-2} M) and 1.0 ml. of Co^{60} (carrier free) solution were taken and, after adjusting the pH and diluting to 20 ml., cobalt chelate was extracted as above. A 2.0 ml. of aqueous layer was then pipetted out into a small stainless dish. The solution was evaporated completely to dryness and the counts were determined using Geiger Counter. The per cent extraction was obtained by comparing the counts with that of the standard which was determined similary before extraction.

Zinc.—Zn^{65} was used as tracer. The method of determination for the per cent extracted was quite similar to that for cobalt.

It was found that per cent extracted is more than 99% in all cases under the optimum pH.

Summary

The absorption spectra of 1-hydroxyacridine were obtained both in aqueous and chloroform solution, and the pK_a and the pK_b were determined. The pK_a is slightly greater than that of oxine, and it is suggested that the stability of metal chelate with 1-hydroxyacridine will have values of the same or larger order as that of oxine chelate, because there is a direct relation between the basicity of a chelating agent, as measured pK_a values, and the stability of the chelates it forms, as cited in the literature of Morrison and Friser[9].

The various aspects of solvent extraction using chloroform were then investigated. The optimum pH range on extraction for each element was determined and it was found that the range is narrow as compared with that of the oxine chelate. The per cent extracted was determined and it was found that copper, nickel, cobalt and zinc were almost completely extracted under the conditions investigated.

The authors thank the Ministry of Eduction for the financial support granted for this research.

Department of Chemisty
Faculty of Science
Kyoto University
Sakyo-ku, Kyoto

9) G. H. Morrison and H. Freiser, "Solvent Extraction in Analytical Chemistry", John Wiley & Sons, Inc., New York (1957), p. 26.

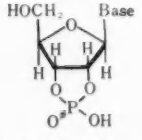
Enzymic Preparation of Guanosine-2', 3'-cyclic Phosphate, Inosine-2', 3'-cyclic Phosphate and Xanthosine-2', 3'-cyclic Phosphate

By Kimiko SATO-ASANO, Yoshiko FUJII and Fujio EGAMI

(Received February 14, 1959)

Our previous studies have shown that ribonuclease T_1(RNase T_1) in Takadiastase hydrolyzes the secondary phosphate ester bonds of guanosine-3' phosphate in ribonucleic acid (RNA)[1-3]. During the digestion, guanosine-2', 3'-cyclic phosphate (G-cyclic-p) is accumulated in the reaction mixture as an intermediary product.

It has been also found that RNase T_1 hydrolyzes *deamino*-ribonucleic acid (*deamino*-RNA) splitting preferentially the secondary phosphate ester bonds of inosine-3' phosphate with an intermediary formation of inosine-2', 3'-cyclic phosphate (I-cyclic-p). With higher amounts of RNase T_1, the secondary phosphate ester bonds of xanthosine-3' phosphate is also hydrolyzed with an intermediary formation of xanthosine-2', 3'-cyclic phosphate (X-cyclic-p)[4].



Nucleoside-2', 3'-cyclic phosphate

1) K. Sato and F. Egami, *J. Biochem.*, **44**, 753 (1957).
2) K. Sato and F. Egami, *Compt. rend. soc. biol.*, **151**, 1792 (1957).
3) K. Sato-Asano, *J. Biochem.*, **46**, 31, (1959).

4) K. Asano and Y. Fujii, *Symposium on Enzyme Chemistry (Japan)*, **10**, 123 (1958).

It has so far been difficult to synthesize G-cyclic-p by a chemical method with good yield and in high purity[5]. Markham et al. prepared G-cyclic-p and adenosine-2', 3'-cyclic phosphate (A-cyclic-p) by mild alkaline hydrolysis of "RNase I core"[6]; however, the yield was far from satisfactory. On the other hand, I-cyclic-p and X-cylic-p have been neither separated from the natural source nor synthesized.

We succeeded in preparing these purine nucleoside cyclic phosphates with good yield by the enzymic reactions. So the method of preparation of these nucleoside-2', 3'-cyclic phosphates and the properties of new compounds will be reported.

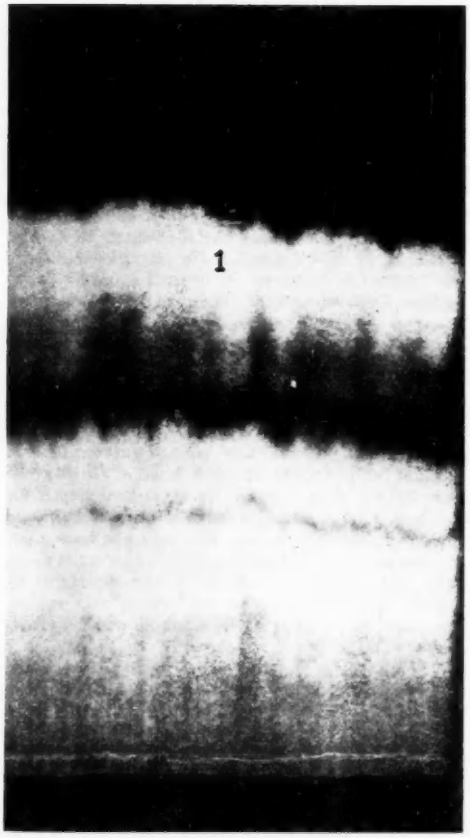


Fig. 1. Paper chromatogram of the dialyzate of the digestion mixture of yeast RNA by RNase T_1. Reaction mixture contains 100 mg. of yeast RNA and 10 μg. of RNase T_1 at pH 7.5. The band 1 is that of G-cyclic-p. Solvent I was used.

Experimental

RNA.—A commercial yeast RNA (Schwarz Laboratories) was deproteinized with chloroform gel formation, dialyzed in a cellophane tubing against distilled water and precipitated with alcohol.

Deamino-RNA.—Yeast RNA was deaminated by the method of Takemura[7]. Details of the preparation and properties of deamino-RNA will be reported elsewhere.

RNase T_1.—The purest sample extracted and prepared from Takadiastase according to the method of Sato and Egami[1] was used.

Paper Chromatography.—*Solvent I*: isopropanol: water (7 : 3) with concentrated aqueous ammonia in the bottom of the vessel (0.5 ml. for each liter of gas phase)[8], descending for 18 to 19 hr.

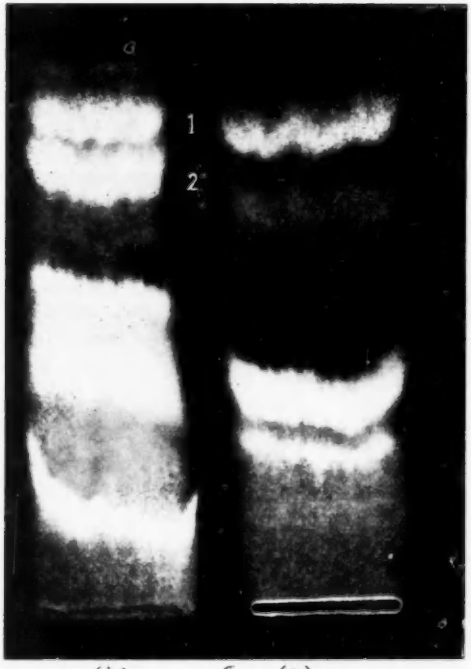


Fig. 2. Paper chromatograms of the dialyzate of the digestion mixture of *deamino*-RNA by RNase T_1. Solvent I was used. The bands are: 1, I-cyclic-p; 2, X-cyclic-p.
a) 20 mg. *deamino*-RNA, 2 μg. RNase T_1/ml.
b) 200 μg. RNase T_1 was added to the nondialyzable fraction in a).

5) D. M. Brown, D. I. Magrath and A. R. Todd, *J. Chem. Soc.*, **1952**, 2708.
6) R. Markham and J. D. Smith, *Biochem. J.*, **52**, 552 (1952); L. A. Heppel and P. R. Whitfeld, ibid., **60**, 1 (1955).
7) S. Takemura, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **72**, 674 (1951).
8) R. Markham and J. D. Smith, *Biochem. J.*, **52**, 558 (1952).

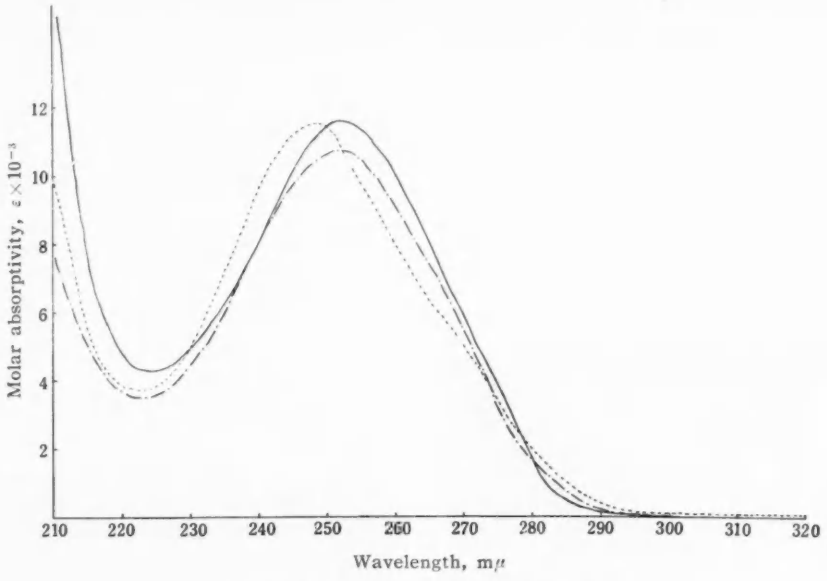


Fig. 3. Absorption spectra of I-cyclic-p.
——, pH 11.2; ------, pH 6.0; — — —, 2 N HCl.
Beckman spectrophotometer type DK2 was used.

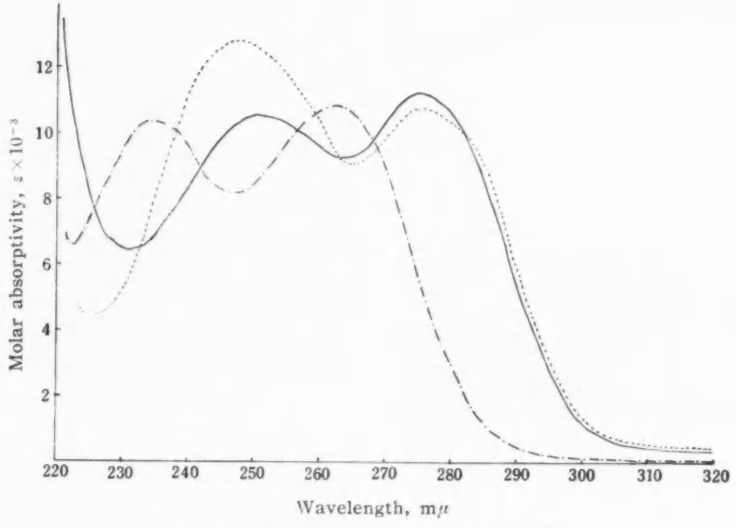


Fig. 4. Absorption spectra of X-cyclic-p.
——, 1 N NaOH; ------, pH 8.1; — — —, pH 3.0.
Beckman spectrophotometer type DK2 was used.

Solvent II: saturated ammonium sulfate : water: isopropanol (79 : 19 : 2)[9], ascending for 9 hr. Tôyôroshi No. 51 paper was used throughout the studies and the bands on the chromatogram were located by the usual photographic methods.

Organic Phosphorus.—It was measured by the method of Allen[10].

Preparation of G-cyclic-p.—Yeast RNA (100 mg.) was dissolved in 5 ml. of distilled water and pH was adjusted to 7.5. To the solution 10 μg. of RNase T_1 was added. The reaction mixture was incubated at 37°C for 2 hr., then dialyzed against distilled water in a cold room under stirring overnight. The dialyzate was concentrated and subjected to paper chromatography (15~20 cm./100 mg. RNA) using solvent I. As is shown in Fig. 1 the wide intensive band 1 was found, this was identified with that of G-cyclic-p[3]. The band was eluted and lyophilyzed. G-cyclic-p was obtained in an almost pure state by chromatography. After the preparation was rechromatographed with the same solvent, it was proved by another paper chromatography test, paper electrophoresis and its U. V. absorption spectrum that it became completely free from other nucleotides except for a trace amount of guanylic acid (Gp).

Preparation of I-cyclic-p.—One handred milligrams of *deamino*-RNA was dissolved in 5 ml. of distilled water at pH 7.5 and 10 μg. of RNase T_1 was added, then the reaction mixture was incubated for 5 hr. at 37°C. The reaction mixture was dialyzed against 50 ml. of distilled water in a cold room under stirring, then the dialyzate was concentrated and subjected to paper chromatography (solvent I, descending for 18 hr.). After drying, the paper was rechromatographed with the same solvent for 19 hr. (Fig. 2a). The broad band 1 moving rapidly was identified with that of I-cyclic-p[11]. Band 2 which is that of X-cyclic-p[11] also appeared sightly. Band 1 was eluted with distilled water, the eluate was concentrated and subjected to paper chromatography using solvent I. There was nothing except for a large amount of I-cyclic-p and a trace of inosinic acid (Ip). It was also proved by another paper chromatography test using solvent II that the band was pure I-cyclic-p. The purest preparation was used for the following experiments.

Preparation of X-cyclic-p.—After the pH of the reaction mixture, which remained in the cellophane tubing in the experimental for I-cyclic-p, was adjusted to 7.5, 1.0 ml. of RNase T_1 (1.3 mg./ml.) was added and the reaction mixture was incubated for 5 hr. at 37°C. Then it was dialyzed against 60 ml. of distilled water in a cold room under stirring, then the dialyzate was concentrated and subjected to paper chromatography (solvent I, descending for 18 hr.). After drying, the paper was rechromatographed with the same solvent for 19 hr. (Fig. 2b). The broad band 2 was identified with that of X-cyclic-p[11]. To purify the sample completely, band 2 was eluted with distilled water, the eluate was concentrated and subjected to rechromatography with the same solvent. There was nothing but large amounts of X-cyclic-p and a trace of xanthylic acid (Xp). Moreover, this band 2 was proved to be pure X-cyclic-p by another paper chromatography test with solvent II. This sample was used in the following studies.

Results and Discussion

Yields.—The yields were calculated from the optical density. Five milligrams G-cyclic-p from 100 mg. of yeast RNA ; 2 mg. of I-cyclic-p from 100 mg. of *deamino*-yeast RNA ; 2.5 mg. of X-cyclic-p from 100 mg. of *deamino*-yeast RNA.

Absorption Spectra of I-cyclic-p and X-cyclic-p.—Using the purest preparation, their ultraviolet absorption spectra were measured at various pH ranges, and their molar extinction coefficients were determined by measuring phosphate (Figs. 3 and 4).

Rf values were calculated in two solvent systems.

TABLE 1. *Rf* VALUES OF PREPARED CYCLIC NUCLEOTIDES AND OF MONONUCLEOTIDES

	Solvent I	Solvent II
G-cyclic-p	0.28	0.29
I-cyclic-p	0.43	0.33
X-cyclic-p	0.35	0.19
A-cyclic-p	0.48	0.13
C-cyclic-p, U-cyclic-p	0.50	0.54
Gp	0.13	0.45 (3') 0.54 (2')
Ip	0.16	0.52
Xp	0.15	0.33
Ap	0.21	0.23 (3') 0.33 (2')
CP, Up	0.21	0.73

These cyclic nucleotides, especially G-cyclic-p, were rather labile in diluted solution and were hydrolyzed to nucleotides. So all procedures had to be carried out as rapidly as possible.

If two or more cyclic nucleotides were produced from RNA at the same time, the separation might be very difficult. So the stepwise enzymic preparation seems to be a better method. After the preparation of G-cyclic-p from the dialyzate of the digestion mixture of yeast RNA by RNase T_1, the nondialyzable fraction which remained in the cellophane tubing was treated in 0.1 N hydrochloric acid to split the residual cyclic phosphate[2], neutralized and dialyzed completely. What may be

9) R. Markham and J. D. Smith, ibid., **49**, 401 (1951).
10) R. J. Allen, ibid., **34**, 858 (1940).
11) K. Sato-Asano and Y. Fujii, *J. Biochem.*, in press.

called "RNase T_1 core" thus obtained was useful for the preparation of pyrimidine nucleosidecyclic phosphates by RNase I.

Pyrimidine nucleosidecyclic phosphates were prepared from the dialyzate of yeast RNA digests by RNase I and the residues were further completely digested and dialyzed, and thus the well known "RNase I core" was obtained. It was also a good source for the preparation of G-cyclic-p by RNase T_1.

It was rather difficult to separate a large amount of I-cyclic-p and X-cyclic-p. To solve this difficulty RNase T_1 digestion was divided into two steps: at the first step with a small quantity of RNase T_1, the greater part of I-cyclic-p was separated and at the second step by addition of more RNase T_1, the remaining I-cyclic-p and X-cyclic-p were obtained separately.

Summary

By RNase T_1 digestion, guanosine-2',3'-cyclic phosphate was obtained with good yield from yeast RNA, and two new compounds, inosine-2',3'-cyclic phosphate and xanthosine-2',3'-cyclic phosphate were obtained from *deamino*-yeast RNA. The properties of the new compounds were studied.

We acknowledge the gift of "Taka-diastase Sankyo" by the Sankyo Pharmaceutical Co., Ltd. The expense of this study was defrayed in part by a grant from the Ministry of Education.

Department of Chemistry
Faculty of Science
Nagoya University
Chikusa-ku, Nagoya

Recombination of Hydrogen, Nitrogen and Oxygen Atoms on Copper and Silver Single Crystal Surfaces

By Kazuo NAKADA

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Hoping to get information about the bond strength of the chemisorption of hydrogen, the author et al.[1] carried out the recombination of hydrogen atoms on various metal surfaces including single crystal surfaces of copper. In the present work, experiments have been extended to cases of nitrogen and oxygen atoms on single crystal surfaces of copper and silver, considering the fact that comparatively simple electronic band structures of copper and silver will render the theoretical treatment of results possible in future. With regard to oxygen atoms, experiments were conducted only on single crystal surfaces of silver, because the probable formation of relatively thick oxide layers on copper surfaces might complicate the subject for consideration.

Since relatively much information about physical and physico-chemical properties of single crystal surfaces of metals with definite crystal indices are available, execution of any surface reaction on these surfaces seems to be advantageous in considering the mechanism of surface reaction through the comparison of catalytic activity with physical properties. With regard to the research along this line, the works of Gwathmey et al.[2], Sosnovsky[3] and Crocker et al.[4] are noteworthy.

However, few works have yet been undertaken except for the work of Gwathmey et al. in which detailed structures of surfaces during the course of and after the completion of the reaction are fully followed. In the work of Sosnovsky, where the decomposition of formic acid on single crystal surfaces of silver was dealt with, the natural free

1) K. Nakada, T. Sugiura and S. Shida, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **76**, 64 (1955); S. Sato, K. Nakada and S. Shida, ibid., **76**, 1308 (1955); K. Nakada, S. Sato and S. Shida, *Proceedings of the Japan Academy*, **31**, 449 (1955); K. Nakada, This Bulletin, **32**, 809 (1959).

2) R. E. Canningham and A. T. Gwathmey, *J. Am. Chem. Soc.*, **76**, 391 (1954).

3) H. M. C. Sosnovsky, *J. Chem. Phys.*, **23**, 1486 (1955).

4) A. J. Crocker and A. T. B. Robertson, *Trans. Faraday Soc.*, **54**, 931 (1958).

surface frozen from the melt was used as a reaction surface. The work of Crocker et al. in which the decomposition of formic acid on single crystal surfaces of copper was dealt with and that of Nakada et al. in which the recombination of hydrogen atoms on the same was dealt with were only concerned with the electropolished surfaces. Although the flatness of these surfaces on the atomic scale was ensured by Rhodin[5] through the adsorption experiment by the use of microbalance technique, there seems still to be doubtful whether or not the electro-polishment would really give such an extreme flatness.

Accordingly, it is highly desirable to know detailed structures of surfaces on which the experiments were made. In the present work, the author devotes himself to the detection of the effect of various kinds of surface pre-treatments on catalytic activity. It seems probable that surfaces subject to such a treatment as chemical etching, which possibly roughen them, will comply with the purpose of this work better than the flattened surfaces, because for such a roughened electron diffraction technique may give the most detailed information on its surface structure. Conversely, it may be expected that from the change in activity resulting from various surface treatments, unknown surface structures lying beyond the limit of the power of the present scientific method, like electron microscopy or electron diffraction technique, would be made clear.

Experimental

An effusion method used in the preceding report* for determining the recombination activity of different transition metals was also adopted this time.

Apparatus. — The apparatus (not shown) described in the above was used without modification, but the sample metal slice was hung only with a Pt/Pt-Rh thermocouple (0.1 mm. in diameter) without any other lead.

Sample Gases.—The hydrogen, oxygen and nitrogen used were all commercial cylinder gases. Hydrogen or oxygen was allowed to bubble through a saturated sodium hydroxide solution and further to diffuse over the platinized asbestos (ca. 400°C) to remove oxygen and hydrogen included in hydrogen and oxygen as an impurity, respectively, but for nitrogen this procedure was not done. They were sent to the discharge tube through a capillary from a reservoir in which the gases were allowed to stay over the saturated sodium hydroxide solution to keep the humidity constant.

Sample Metal Slices.—Single crystals of copper and silver were produced by means of a slow cooling method from electrolytic copper and standard silver for analysis respectively. The single crystals thus obtained were of a cylindrical form (12 mm. in diameter and about 6 cm. long). Single crystal slices (generally in an elliptical form, about 2 to 3 mm. thick) were cut from a cylindrical single crystal in order that their macroscopic-cut planes might coincide with the three principal planes (100), (110) and (111), but in the case of silver only the (110) and (100) slices were prepared.

Pre-treatment of Surfaces.—Two surfaces of a sample slice were generally subjected to two different kinds of pre-treatments, e. g., one pre-treatment was electro-polishment and another, chemical etching with nitric acid or the like. The main conditions of pre-treatment adopted in this work were as follows:

1) Chemical etching was carried out a) in the nitric acid solution (1 : 1 by volume) for 3 min. and b) in the saturated ammonium persulfate solution for 15 min.

2) Electro-polishment of copper was done in the bath of phosphoric acid (90%) at the current densities of 6 to 8 amp./dm^2 for 10 min. and that of silver in the mixed solution of potassium cyanide (10%) and potassium ferrocyanide (10%) at the current densities of 1 to 3 amp./dm^2 for 3 min.

3) For the electric plating, solutions of potassium cuprous cyanide, potassium silver cyanide and ammonium aurocyanide were used as baths of copper-, silver- and gold-plating, respectively.

Procedure.—All free atoms were produced in a discharge tube by use of alternating currents. A sputtering of the electrode material (aluminum) occurred more markedly in the case of nitrogen than in oxygen. Since such a sputtering was localized within the neighborhood of electrodes even in the case of nitrogen, they did not become a serious obstacle to the present experiments.

In the reaction chamber, which was strongly pumped off, the sample metal slice was hung only by a Pt/Pt-Rh thermocouple (0.1 mm.) serving as the temperature measurements at the front of a small hole provided at the end of a side tube of the discharge tube. The temperature of a sample can be followed by measuring the electro-motive force by use of a K-type potentiometer. The electro-motive force was read at intervals of 5 min. The slice was allowed to turn over every twenty or thirty minutes. Before and after this procedure, the temperature was usually shifted from one value to another. From such a shift of the temperature the difference in activities of two surfaces of the same sample subjected to different treatments could readily be detected.

Results

In Fig. 1 is given a plot of temperature, expressed in terms of electro-motive force

5) T. N. Rhodin, *J. Am. Chem. Soc.*, **72**, 5691 (1954).

* This Bulletin, loc. cit. in Ref. 1.

TABLE I. INEQUALITY RELATIONS OF CATALYTIC ACTIVITY

No.	Species of slice	Method of pre-treatment		Inequality relation	Kinds of atoms
		One side	The other side		
1	Cu(100)	El. pol. : H_3PO_4	Mech. pol. 06 emery paper	Mech. pol.>El. pol.	N
2	Cu(100)	ditto	Chem. etch. : HNO_3	El. pol.>Chem. etch.	N
3	Cu(100)	Chem. etch.: HNO_3	Chem. etch. : $(NH_4)_2S_2O_8$	$HNO_3<(NH_4)_2S_2O_8$	N, H
4	Cu(110)	El. pol. : H_3PO_4	Mech. pol. 06 emery paper	Mech. pol.>El. pol.	N
5	Cu(110)	ditto	Chem. etch. : HNO_3	El. pol.>Chem. etch.	N
6	Cu(110)	Chem. etch.: HNO_3	Chem. etch. : $(NH_4)_2S_2O_8$	$HNO_3>(NH_4)_2S_2O_8$	N, H
7	Cu(110)/ poly.	Chem. etch. : HNO_3, single	Chem. etch. : HNO_3, poly.	poly.>single	N
8	Cu(110)/ poly.	Chem. etch. : $(NH_4)_2S_2O_8$, single	Chem. etch. : $(NH_4)_2S_2O_8$, poly.	poly.>single	N
9	Cu(111)	El. pol. : H_3PO_4	Chem. etch. : HNO_3	El. pol.>Chem. etch.	N, H
10	Cu(111)	Chem. etch., HNO_3	Chem. etch. : $(NH_4)_2S_2O_8$	$HNO_3<(NH_4)_2S_2O_8$	H
11	Cu(111)	El. pol. : $CuSO_4$	El. pol. : H_3PO_4	$CuSO_4\simeq H_3PO_4$	H
12	Ag(100)	El. pol. : $KCN+K_4FeCN_6$	Chem. etch. : HNO_3	El. pol.>Chem. etch.	H
13	Ag(100)	ditto	Chem. etch. : $(NH_4)_2S_2O_8$	El. pol.$\simeq$Chem. etch.	H
14	Ag(100)	ditto	Cu, Ag and Au-plating	(100)>Cu, Ag and Au	H, N
15	Ag(110)	ditto	ditto	(110)>Cu, Ag and Au	H, N
16	Ag(110)	Chem. etch.: HNO_3	Cu-plating	(110)>Cu	H, N
17	Ag(100)	El. pol. : $KCN+K_4FeCN_6$	Cu, Au-plating	Cu, Au>(100)	O
18	Ag(110)	ditto	ditto	(110)>Cu, Au	O

In this table the following abbreviations were adopted. For example, chemical etching in a nitric acid solution was abbreviated as Chem. etch. :HNO_3, electrolytic polishing as El. pol. :H_3PO_4 and electrical plating of silver as Ag-plating.

(μV), against the time (min.) for the case of Ag(110) slice, one side of which is the one electrically plated with silver, while the other side is electrolytically polished. Arrows in Fig. 1 show times when the sample slice was let turn over. From this plot the electrolytically polished Ag(110) surface is found to be more active than the electrically plated silver surface.

Inequality relations thus determined are shown en bloc in Table I. The first column shows species of macroscopic-cut planes of sample slices. In the second and the third columns are shown methods of pre-treatments applied to each side of the surfaces. In the fourth column are given the inequality relations about recombination activities of two surfaces. The last column shows kinds of atoms used.

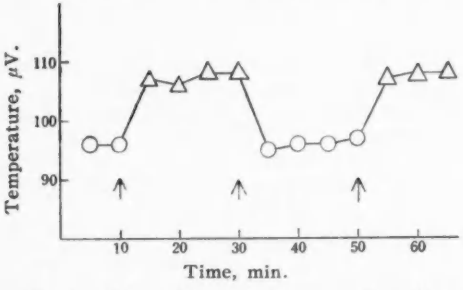


Fig. 1. The shift of the sample slice temperatures on the alternative exposure of two side planes to the reacting gas. This is an example about silver slice corresponding to Table I, No. 15.
○: Silver plating
△: Electrolytic polishing

Some Remarks on the Surface Structures

Since the main purpose of the present work is to make clear the effect of different surface structures on catalytic activity, several bits of information available to date concerning the surface structures of single crystals of some metals will be reviewed below in a little detail.

Among the works along this line the work of Yamaguchi[6] on single crystals of nickel is noteworthy. He made clear their detailed structures when they were etched by a mixed solution of ethyl alcohol and liquid bromine (1 : 1 by volume) by the cooperative uses of electron microscope and electron diffraction technique. In a similar way, structures of the single crystal of copper etched with ammonium

6) S. Yamaguchi, *J. Appl. Phys.*, **22**, 983 (1951).

persulfate was made clear by Ueda et al.[7] According to their result, the surface of a single crystal of copper etched by the saturated solution of ammonium persulfate exposes composite small facets, but all the faces of such facets have (110) family index irrespective of their directions.

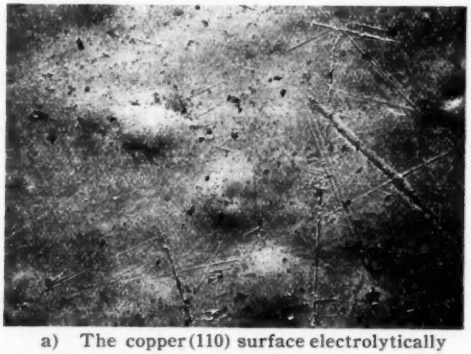
Chalmers et al.[8] examined the surface thermally etched in the presence of oxygen or nitrogen. According to their results, the surface heated to 500°C in oxygen was found to show a zonal orientation which should be ascribed to the exposition of (111) face, while surfaces heated in nitrogen show a flat surface having all desired orientations. Pashley[9] examined the single crystal surfaces of silver parallel to the (100), (111), (110) and (311) plane when they were subjected to the electrolytic etching, electrolytic polishing and chemical etching by nitric acid (35%). In this work the electrolytic polishing was found to give very smooth surfaces, while the electrolytic etching or the chemical etching to give well-developed facets which were always of the (100), (110), (210) and (310) types and did not include (111) facets.

Less detailed and less reliable information can be drawn from the optical back reflection image obtained when a very intense light beam is spotted on the single crystal surfaces etched by chemical agents. This optical back reflection method was used in determining the crystal axes of single crystals in this work. Several pieces of information obtained by the use of this method can be found in old works of physicists who were engaged in the study of the anisotropy of work functions of metal single crystals. Farnsworth[10] found that the electrolytic etching of a single crystal of copper at low current densities developed a (111) face and the same treatment at high current densities a (100) face. In the work of Rose[11] the electrolytic etching of the (111) surface in a copper sulfate solution was stated to expose a (111) face and the chemical etching of the (100) surface in a nitric acid solution (65%) to produce a smooth (100) surface with very few undesired faces.

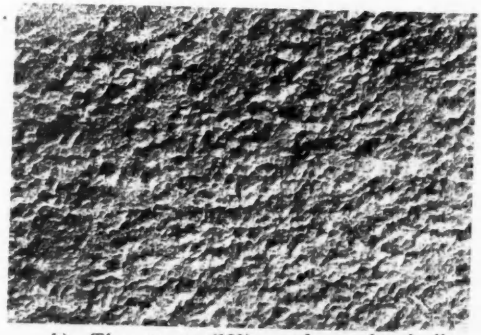
7) R. Ueda et al., presented at the Meeting of the Physical Society of Japan, Osaka, November 2, 1953 (unpublished).
8) B. Chalmers, R. King and R. Shuttleworth, *Proc. Roy. Soc.*, **A192**, 465 (1948).
9) D. W. Pashley, *Proc. Phys. Soc.*, **A64**, 1113 (1951).
10) H. E. Farnsworth, *Phys. Revs.*, **40**, 684 (1932).
11) B. A. Rose, ibid., **44**, 585 (1933).

Discussion

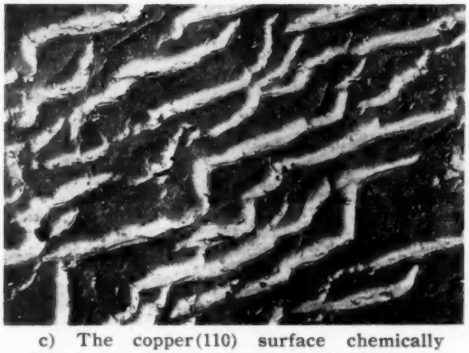
In Fig. 2 is given only a part of the electron micrographs of single crystal surfaces of copper and silver with different crystal indices. From Figs. 2b, c and d, it was clearly recognized that slices with different crystal indices were subjected to corrosion in a considerably different



a) The copper(110) surface electrolytically polished in a phosphoric acid solution (×2000).



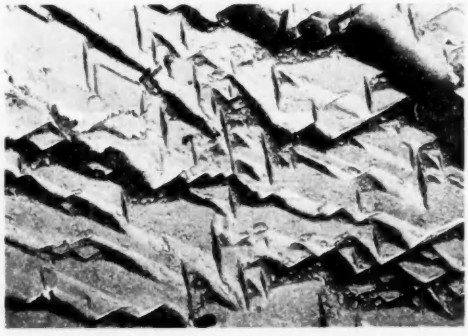
b) The copper(100) surface chemically etched in a nitric acid solution (×3500).



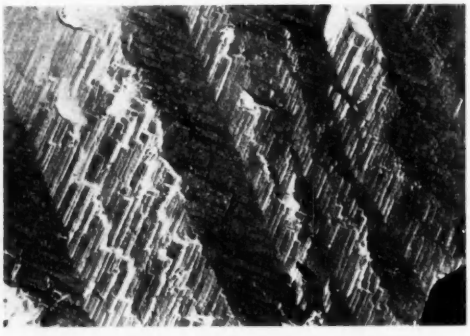
c) The copper(110) surface chemically etched in a nitric acid solution (×3500).

d) The copper(111) surface chemically etched in a nitric acid solution (×3500).

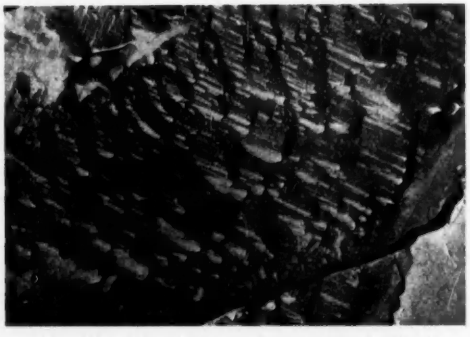
g) The silver(100) surface chemically etched in a nitric acid solution (×3500).



e) The silver(100) surface electrolytically polished in a mixing solution of potassium cyanide and potassium ferrocyanide (×3500).



h) The silver(110) surface chemically etched in a nitric acid solution (×3500).



f) The silver(110) surface electrolytically polished in the same bath as in e) (×3500).

i) The electro-polished silver(110) surface aged under contact with oxygen atoms(×3500).

Fig. 2. Electron micrographs of copper and silver single crystal surfaces subjected to various kinds of pre-treatment.

manner on the attack of the same etching agent. As known from Figs. 2e and f, it seems rather reasonable that the electrolytical polishing of silver surfaces in the bath used in the present work is considered as the electrolytical etching in an electron-microscopic scale. In spite of the significance of determining crystallographic planes of the small facets exposed to the reacting gas, further approach to the true surface structures could not be attained without getting an opportunity to use the electron diffraction method.

No results were obtained in which inequality relations of relative activities for hydrogen atoms and nitrogen atoms disagreed with each other. This suggests that the recombination of hydrogen atoms and nitrogen atoms may proceed probably through the similar mechanism.

In the case of both Cu(100) and Cu(110) slices, the mechanically polished surfaces were more active than electrolytically polished surfaces (Table I, No. 1 and 4). It is supposed that this difference in activity might have originated in strains of Beilby layers formed on the surface. Experiments of No. 7 and 8 were made about the special sample of the Cu(110) slice, the back side of which was changed to a polycrystal state by rapid cooling of only one side after re-heating, while another side remained to be the original single crystal state. From the comparison of activities of these two surfaces for the recombination of nitrogen atoms, both of which are subjected to the attack of the same reagent (nitric acid or ammonium persulfate), were obtained results showing that the polycrystal surface was always more active than the single crystal surface. It seems, however, to be premature to accept the existence of the effect of the crystal boundaries on the catalytic activity.

Bearing in mind the statement of Rose, an experiment of No. 11 was done to know whether the Cu(111) surface electrolytically polished in a copper sulfate solution may be more flat (accordingly less active) than the electrolytically polished surface in phosphoric acid, but any difference in these two treatments could not be detected.

In the previous work of the present author et al. about the recombination of hydrogen atoms on single crystal surfaces of copper which was electrolytically polished, it was made clear that the (110) face is the most active, the (100) face less active than this, and the (111) face the least active. In view of Ueda's work cited above, in which single crystal surfaces of copper etched by ammonium persulfate were shown to be composed of only the (110) family facets, it may be expected that surfaces etched by ammonium persulfate will be more active than those etched by nitric acid which was known to develop the (100) face. Present results show that with the Cu(100) slice this is certainly the case (No. 3), whereas with the Cu(110) slice the reverse order of activity has been obtained (No. 6). These results show that copper surfaces subjected to the chemical etching by nitric acid or ammonium persulfate seem to have more complex structures than expected from the information given above.

Throughout every three slices (100), (110) and (111), electrolytically polished surfaces were found always to be more active than chemically etched surfaces (No. 2, 5 and 9). This suggests that there may exist some other faces with relatively high activity than these principal faces. It is instructive that chemically etched surfaces having a rather complex microtopography are less active than flat surfaces electrolytically polished. This implies that the recombination does not proceed on the corners or edges of small crystal facets, but rather mainly on plane faces. This has probably originated in such a special circumstance as that reactants are only composed of free atoms which need not be activated further.

Next, let us examine the results on single crystal surfaces of silver. As for the Ag(100) slice, surfaces chemically etched by nitric acid are also less active than those electrolytically polished in accord with the experiment of No. 2 (No. 12), whereas between surfaces chemically etched by ammonium persulfate and those electrolytically polished, no difference in activity was observed (No. 13). Combining the result of the experiment No. 12 with that of No. 13, the surface etched by ammonium persulfate is known to be more active than the one etched by nitric acid in accord with experiment No. 3 about copper. Consequently, it may be said that these chemical agents will have, to some extent, a similar corrosive action against both copper and silver.

For both the recombination of hydrogen atoms and that of nitrogen atoms, Ag(100) and Ag(110) surfaces electrolytically

polished were together more active than the electrically plated surfaces of copper, silver and gold (No. 14 and 15). This shows firstly that activities of these three kinds of metals do not show any wide diversity and secondly that the character of surfaces plays a significant role when the activities of these metals were compared. From the combination of No. 14 and 15, no conclusion could be drawn as to which of the Ag(110) slice and the Ag(100) slice would be more active. With reference to the earlier results of the present author et al. about the recombination of hydrogen atoms on single crystal surfaces of copper, the author has been inclined to ascribe the higher activity to the (110) face.

For the recombination of oxygen atoms on single crystal surfaces of silver subjected to the electro-polishment, inequality relations

$$\text{Ag}(110) > \text{Cu or Au plated surface} > \text{Ag}(100)$$

were obtained (No. 17 and 18). The relation Ag(110)>Ag(100) is in good accordance with the case of the recombination of hydrogen atoms on single crystal surfaces of copper so far as the order is concerned. This accordance seems, however, to be fortuitous in view of the considerably larger nuclear distance of an oxygen molecule, 1.20 Å, than that of a hydrogen molecule, 0.75 Å, even though the larger lattice constant of silver, 4.08Å, compared to that of copper, 3.61 Å, would work favorably for this reaction.

With the recombination of oxygen atoms it was noticed that a kind of polishing action becomes appreciable in repeated runs. Comparing the micro-photograph of Fig. 2a with Fig. 2i, it is immediately perceived that such an aged surface under the contact with oxygen atoms resembles the electrolytically polished surface of copper in its micro-topographic appearance, except that the former possesses somewhat worse flatness than the latter. Experiments No. 17 and 18 are obtained with respect to such aged surfaces, while experiments No. 12 to No. 15 with respect to surfaces polished afresh.

Though it appears probable that this kind of polishing will come from any particular property of oxide layers, such changes of surface structures were not studied further, because this problem is not concerned with the main theme of the present work.

Summary

Recombination of hydrogen atoms, nitrogen atoms and oxygen atoms was carried out on single crystal surfaces of copper and silver subjected to various surface pre-treatments.

With both the recombination of hydrogen atoms and that of nitrogen atoms, copper surfaces electrolytically polished have always higher activity than those chemically polished. The Cu(100) surface chemically etched by ammonium persulfate was more active than that etched by nitric acid for both hydrogen atoms and nitrogen atoms, whereas with the Cu(110) the opposite order of activity was obtained. For both silver and copper, no evidence was found to show the different order of activity between the recombination of hydrogen atoms and that of nitrogen atoms. Concerning the recombination of oxygen atoms on single crystal surfaces of silver, the (110) face was found to be more active than the (100) face in accord with the result of our earlier work about the recombination of hydrogen atoms on single crystal surfaces of copper.

The author wishes to express his gratitude to Professor S. Shida for his help and encouragement during the course of this study.

Laboratory of Physical Chemistry
Tokyo Institute of Technology
Meguro-ku, Tokyo

Polymerization of Methyl Methacrylate Initiated by the System of p-Toluenesulfinic Acid, Dimethylaniline and Oxygen

By Ryoichi UEHARA

(Received December 17, 1958)

Polymerization of vinyl monomers initiated by some sulfinic acids was first reported by Hagger[1]. The present author[2] has reported a self-curing method of methyl methacrylate by the combined action of *p*-toluenesulfinic acid and dimethylaniline in the presence of air. Hagger considered that sulfinic acids by themselves could initiate the polymerization of vinyl monomers and reported an equation representing a relation between the initial rate of polymerization of methyl methacrylate and the concentration of *p*-toluenesulfinic acid.

Recently, Bredereck and others[3] found that absolutely pure *p*-toluenesulfinic acid could not initiate the polymerization of methyl methacrylate, and that for the initiation of the polymerization, the coexistence of oxygen and an "oxygen-acceptor" such as amines or chloide ions was necessary. The polymerization-initiating action of sulfinic acid found by Hagger was explained by Bredereck to be due to the combined action of the sulfinic acid, oxygen in air, and chloride ions containd in the sulfinic acid as an impurity. Moreover, Bredereck[4] has postulated a mechanism for the initiation of the polymerization of methyl methacrylate with an initiating system consisting of oxygen, *p*-toluenesulfinic acid, and an "oxygen-acceptor"; i.e., a peroxide was formed from oxygen and the sulfinic acid, and then a radical was produced from the peroxide and the "oxygen-acceptor" to initiate the polymerization. But no experimental evidence was given by him for this mechanism.

The present author has studied the polymerization of methyl methacrylate initiated by the system of *p*-toluenesulfinic acid, oxygen in air and dimethylaniline from the standpoint of chemical kinetics. In the present paper, correlations of the initial rate of polymerization of methyl methacrylate with the concentration of the components of the inititating system are given, and the initial step of the polymerization is discussed.

The polymerization was carried out in open test tubes under atmospheric pressure of air for the study of the dependence of the initial rate (R) of polymerization upon concentrations of *p*-toluenesulfinic acid (TSA), dimethylaniline (DMA), and methyl methacrylate (MMA). When the effect of the initial pressure of oxygen was tested, the polymerization was carried out in sealed test tubes under various initial pressures of air.

When the concentration of *p*-toluenesulfinic acid was held constant and that of dimethylaniline was varied under atmospheric pressure of air, the initial rate of the bulk polymerization of methyl methacrlate

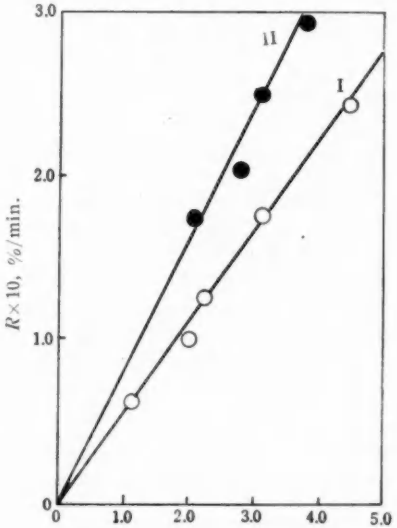


Fig. 1. Correlations of R with $[TSA]^{1/2}$ and $[DMA]^{1/2}$ at 30°C in air.
Line I. $[TSA]=5.1\times10^{-2}$ mol./l.
Line II. $[DMA]=10.0\times10^{-2}$ mol./l.

1) O. Hagger, *Helv. Chim. Acta.*, **31**, 1629 (1948).
2) R. Uehara, *Dental Practice* (*Rinsho Shika*), **196**, 24 (1952).
3) H. Bredereck et al., *Ber.*, **89**, 731 (1956).
4) H. Bredereck et. al., *Angew. Chem.*, **68**, 306 (1956).

was linearly proportional to the square root of the concentration of dimethylaniline. This correlation is shown by line I in Fig. 1, in which 5.01×10^{-2} mol./l. of *p*-toluenesulfinic acid was used at 30°C.

When the concentration of dimethylaniline was kept constant and that of *p*-toluenesulfinic acid was varied, the initial rate of polymerization was linearly dependent upon the square root of the concentration of *p*-toluenesulfinic acid. This relationship is shown by line II in Fig. 1, in which 10×10^{-2} mol./l. of dimethylaniline was used at 30°C. Straight lines I and II in Fig. 1 are brought to a focus at the origin. This fact indicates that neither *p*-toluenesulfinic acid nor dimethylaniline alone can initiate the polymerization in combination with oxygen in air.

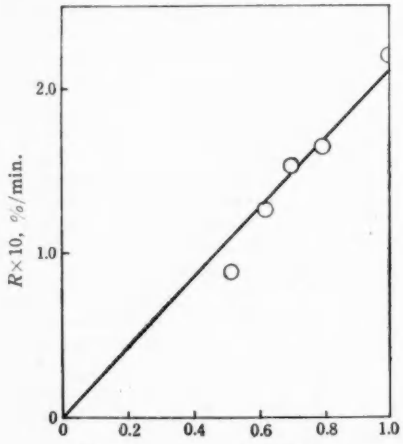


Fig. 2. Correlation of R with the initial pressure of air at 30°C
[TSA]=[DMA]=8.8×10^{-2} mol./l.

In Fig. 2 the correlation of the initial rate of polymerization with the initial pressure of air in the sealed test tubes is shown. The initial rate of polymerization is linearly proportional to the square root of the initial pressure of air. In this case 8.8×10^{-2} mol./l. of both *p*-toluenesulfinic acid and dimethylaniline were used. The straight line in Fig. 2 gose through the origin. This fact indicates that the polymerization can not be initiated without air. The pressure of air is proportional to that of oxygen, so Fig. 2 shows that the initial rate of polymerization is linearly dependent upon the square root of the initial pressure of oxygen.

In the case of the solution-polymerization in benzene, the initial rate of polymerization was linearly dependent upon the concentration of methyl methacrylate. This correlation is shown in Fig. 3, in which 5.10×10^{-2} mol./l. of both *p*-toluenesulfinic acid and dimethylaniline were used at 40°C, under air of atmospheric pressure.

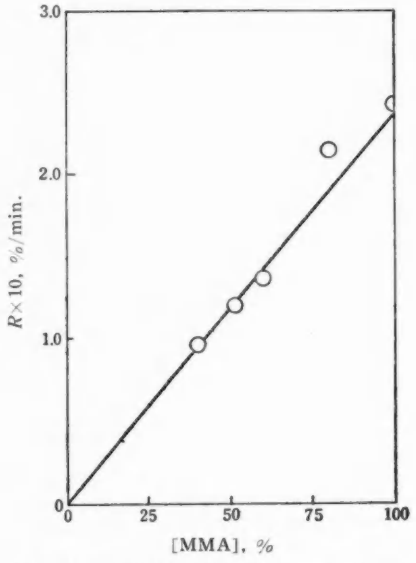


Fig. 3. Relationship between R and [MMA] in case of solution-polymerization in benzene at 40°C.
[TSA]=[DMA]=5.10×10^{-2} mol./l.

Correlations shown in Figs. 1—3 can be represented by the following equation:

$$R=k[O_2]^{1/2}[TSA]^{1/2}[DMA]^{1/2}[MMA] \quad (1)$$

where k is a constant.

Eq. 1 suggests that oxygen, *p*-toluenesulfinic acid and dimethylaniline, all three, take part in the formation of a radical to initiate the polymerization, but methyl methacrylate is not concerned in the radical formation at the initiation reaction. Moreover, Eq. 1 suggests that there may be several reactions forming the radical from the initiating system. As mentioned above, Bredereck[4] has postulated the formation of a peroxide from oxygen and *p*-toluenesulfinic acid as the first step of the initiation. In another paper, however, Bredereck[3] has reported very briefly without any details of experiments that salts of *p*-toluenesulfinic acid and some aromatic amines initiated the polymerization of methyl methacrylate under air. In addition, it has been reported by

Bredereck[5] and Brauer[6] that salts of the sulfinic acid and amines were efficient accelerators for the polymerization of methyl methacrylate initiated with benzoyl peroxide. Formation of a salt from an amine and *p*-toluenesulfinic acid takes place very smoothly in organic solvent[6]. So, in the case of the combination of *p*-toluenesulfinic acid and dimethylaniline, formation of a salt from the sulfinic acid and the amine is more probable than the formation of a peroxide from the sulfinic acid and oxygen in air. The initiating system, *p*-toluenesulfinic acid-oxygen-chloride ions, must be considered separately from the initiating system under discussion.

To get support for this idea from another point of view, the present author has examined the effects of anhydride, and methyl and ethyl esters of *p*-toluenesulfinic acid for the initiation of the polymerization. The per cent conversions of bulk polymerization by means of equimolar mixtures of these compounds and dimethylaniline are shown in Table I.

TABLE I. THE PER CENT CONVERSIONS OF THE BULK POLYMERIZATION OF METHYL METHACRYLTE UNDER ATMOSPHERIC PRESSURE OF AIR

Initiator*	Conversions, % at 30°C		at 70°C	
	3 hr.	6 hr.	1 hr.	3 hr.
p-Toluenesulfinic acid	22.1	98.7	43.8	96.2
Anhydride	0	0	trace	3.8
Methyl ester	0	0	trace	8.4
Ethyl estr	0	0	trace	4.3

* 5.0×10^{-2} mol./l. of each was used together with equimolar amount of dimethylaniline

Polymerizations were carried out at 30 and 70°C under atomospheric pressure of air. At 30°C, *p*-toluenesulfinic acid was the only material which was responsible for the initiating action. At 70°C, the effect of *p*-toluenesulfinic acid was much greater than those of its derivatives. Namely, the polymerization-initiating action of the sulfinic acid was lost by changing it to its anhydride or esters. Therefore, it appears to be conclusive that the formation of a salt from the sulfinic acid and dimethylaniline is the first step of the polymerization.

By considering the formation of the salt, the following reactions of polymerization are derived:

$$\mathrm{TSA}+\mathrm{DMA}\overset{K}{\rightleftarrows}\mathrm{S}$$

$$\mathrm{S}+\mathrm{O_2}\overset{k_1}{\rightarrow}\mathrm{R}\cdot$$

$$\mathrm{MMA}+\mathrm{R}\cdot\overset{k_2}{\rightarrow}\mathrm{P_1}\cdot$$

$$\mathrm{P}_m\cdot+\mathrm{MMA}\overset{k_3}{\rightarrow}\mathrm{P}_{m+1}\cdot$$

$$\mathrm{P}_m\cdot+\mathrm{P}_n\cdot\overset{k_4}{\rightarrow}\mathrm{P}_{m+n}\ \text{or}\ \mathrm{P}_m+\mathrm{P}_n$$

where S is the salt, R· the radical formed from the salt and oxygen, $P_1\cdot$, $P_m\cdot$, $P_n\cdot$, $P_{m+1}\cdot$ are polymer radicals, P_m, P_n, P_{m+n} polymer molecules, K is the euqilibrium constant, and k_1, k_2, k_3, k_4 are respectively rate constants for each of the reactions.

From these reactions the follwing equation can be deduced by the usual method of chemical kinetics for radical polmerization:

$$R=k_3(Kk_1/k_4)^{1/2}[\mathrm{O_2}]^{1/2}[\mathrm{TSA}]^{1/2}[\mathrm{DMA}]^{1/2}[\mathrm{MMA}] \qquad (2)$$

Eq. 2 completely coincides with Eq. 1.

Experimetal

Materials.—Purification of methyl methacrylate, dimethylaniline and benzene have been reported in a previous paper by the present author[7]. *p*-Toluenesulfinic acid was prepared from *p*-toluenediazonium sulfate by using sulfur dioxide and copper[8]. The crude product was washed with distilled water until ions of heavy metals, chloride and sulfate were not detected in the washing then recrystallized from benzene and methanol, and dried under reduced pressure, m.p. 81°C. The crystallization and the drying of the sulfinic acid were carried out as rapidly as possible, and the purified sulfinic acid was used immediately after drying to avoid deterioration. Anhydride of the sulfinic acid was obtained by treating the acid with acetic anhydride in the presence of a small amount of sulfuric acid, m.p. 75.0°C[9]. Methyl and ethyl esters of the sulfinic acid were prepared from sodium *p*-toluenesulfinate and metyl or ethyl chlorocarbonate, respectively[10]. The esters were used without any purification because of their instability.

Polymerization.—Polymerization under atmospheric pressure of air was carried out in test tubes, each of which was open to the atmosphere

5) H. Bredereck et. al., *Makromol. Chem.*, **12**, 100 (1954).
6) G. M. Brauer and F. R. Burns, *J. Polymer Sci.*, **19**, 311 (1956).
7) R. Uehara, This Bulletin, **31**, 685 (1958).
8) L. Gattermann, *Ber.*, **32**, 1136 (1899).
9) E. Knoevenagel, ibid., **41**, 3326 (1908).
10) R. Otto et. al., ibid., **18**, 2506 (1885).

through a capillary at the top. The test tubes were 15 mm. in diameter and 20 cm. in height, and the capillary was 1 mm. in inner diameter and 4 cm. in length, and fitted to the test tube with a ground glass joint. When the effect of the initial pressure of the air was examined, sealed test tubes, each of which was 20 cc. in capacity, were used in place of the above mentioned open tubes. *p*-Toluenesulfinic acid and dimethylaniline were dissolved separately in methyl methacrylate. Both solutions were chilled in a dry ice-methanol bath for 30 min. Measured amounts of each chilled solution were placed in a test tube and mixed. The polymerization was effected by shaking the tubes in a thermostat. The yield of the polymer was measured at intervals of 10 min. Details of the procedures of polymerization and the determination of the initial rate of polymerization have been reported previously[7].

Summary

Initiation of the polymerization of methyl methacrylate with the initiating system, *p*-toluenesulfinc acid-oxygen-dimethylaniline, has been investigated from the standpoint of chemical kinetics. The initial rate of polymerization of methyl methacrylate was linearly proportional to the square roots of the concentrations of each component of the initiating system, and methyl methacrylate. The polymerization initiating action of the initiating system is lost by changing the sulfinic acid to its anhydride or esters. The formation of a salt from the sulfinic acid and dimethylaniline was suggested as the first step of the initiation of the polymerization.

The present author wishes to express his hearty thanks to Professor Osamu Simamura of the University of Tokyo for his interest in this work.

Tama Kagaku Kogyo Co.
2-28 Minamirokugo
Ota-ku, Tokyo

Polymerization of Methyl Methacrylate Initiated by a Combined Action of p-Tolyl Methyl Sulfone, Dimethylaniline and Oxygen in Air

By Ryoichi UEHARA

(Received December 25, 1958)

p-Tolyl methyl sulfone first reported by Knoevenagel[1] is a compound prepared from sodium *p*-toluenesulfinate and methyl iodide, and an isomer of methyl *p*-toluenesulfinate. The effect of *p*-toluenesulfinic acid for the polymerization of methyl methacrylate has been noted by several authors[2] and that of *p*-tolyl hydroxymethyl sulfone has been reported by Bredereck[3], but about the effect of *p*-tolyl methyl sulfone nothing has been reported up to the present.

It has been found by the present author that the polymerization of methyl methacrylate was initiated by a combined action of *p*-tolyl methyl sulfone, dimethylaniline and oxygen in air. The fact that the system of *p*-toluenesulfinic acid, dimethylaniline and oxygen lost the ability to initiate the polymerization by changing the sulfinic acid to its esters has been reported in a previous paper by the present author[4]. So, it appears of interest that the isomer of the methyl ester initiates the polymerization in combination with dimethylaniline and oxygen. In the present paper, some experimental results concerning the relation between the per cent conversion of the polymerization and the concentrations of the initiating reagents, and effects of various amines on the initiating ability of the system are given. In Fig. 1, per cent conversions versus time of the bulk polymerization of methyl methacrylate in air at 70°C are shown. The concentrations of *p*-tolyl methyl sulfone (TMS) and dimethylaniline (DMA) were respectively 3.01×10^{-2} and 2.98×10^{-2} mol./l. In the case when *p*-tolyl methyl sulfone alone was used

1) E. Knoevenagel, *Ber.*, **21**, 1349 (1888).
2) For example, H. Bredreck et. al., ibid., **89**, 731 (1956).
3) H. Bredereck et. al., *Makromol. Chem.*, **12**, 100 (1954).
4) R. Uehara, This Bulletin, **32**, 1079 (1959).

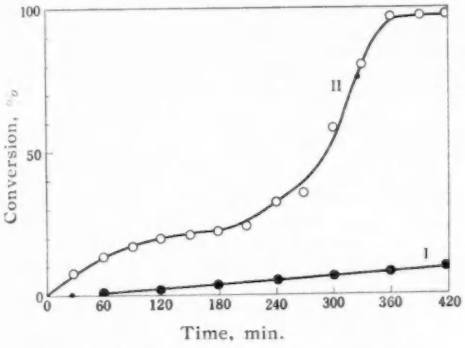


Fig. 1. Conversion versus time relationships of the bulk polymerization at 70°C in air.
([TMS] = 3.01×10^{-2}, [DMA] = 2.98×10^{-2} mol./l., I. TMS alone, II. TMS and DMA).

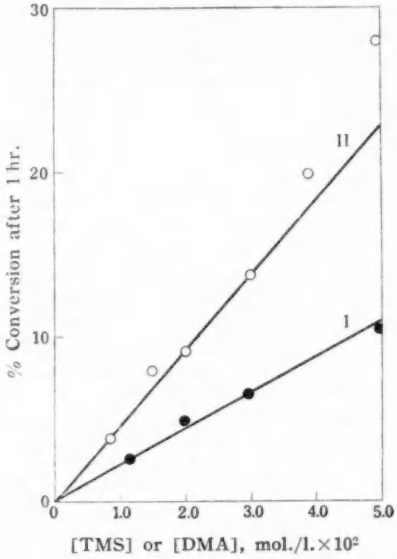


Fig. 2. Correlations of % conversion after 1 hr. with concentration of the initiating reagent.
(I, at 60°C, II, at 70°C)

under air, an induction period appeared and then the polymerization took place at a very small rate. When dimethylaniline was used alone, trace of polymethyl methacrylate was formed after 3 hr. By means of *p*-tolyl methyl sulfone and dimethylaniline, the polymerization proceeded at a fairly rapid rate under air. In that case, the time-conversion curve shows an *S*-form which appears usually in the bulk polymerization of methyl methacrylate. The polymerization was completely inhibited by the addition of 0.10×10^{-2} mol./l. of hydroquinone. Under nitrogen the polymerization did not take place.

When equimolar mixture of *p*-tolyl methyl sulfone and dimethylaniline were used in air, per cent conversion after 1 hr. at 60°C were linearly proportional to the initial concentration of *p*-tolyl methyl sulfone or dimethylaniline. At 70°C, the linear dependence of the per cent conversion upon the concentration of *p*-tolyl methyl sulfone can be seen in case the initial concentration of *p*-tolyl methyl sulfone is less than 3.0×10^{-2} mol./l. Those correlations are shown in Fig. 2.

In Table I, per cent conversions after 1 hr. (at 70°C) in the bulk polymerization of methyl methacrylate initiated by equimolar mixtures of *p*-tolyl methyl sulfone and various amines are shown. The mixtures containing heterocyclic, aliphatic, primary and secondary amines were not responsible for the initiation of the polymerization. Only aromatic tertiary amines were effective as the component of the polymerization-initiating system. *p*-Substitution in dimethylaniline influenced significantly its efficiency as a component of the initiating system. Electron-donating groups such as methyl and methoxy increased the yield of the polymer, while electron-withdrawing groups such as chlorine and bromine reduced the yield. When a strongly electron-withdrawing group such as nitro, nitroso, or phenylazo

TABLE I. THE PER CENT CONVERSIONS AFTER 1 HR. AT 70°C IN AIR

Amine*	% Conversion
Dimethylaniline	14.5
N,*N*-Dimethyl-*p*-anisidine	31.3
N,*N*-Dimethyl-*p*-toluidine	26.9
N,*N*-Dimethyl-*p*-chloroaniline	6.03
N,*N*-Dimethyl-*p*-bromoaniline	5.86
N,*N*-Dimethyl-*p*-nitrosoaniline	0
N,*N*-Dimethyl-*p*-nitroaniline	0
N,*N*-Dimethyl-*p*-phenylazoaniline	0
Aniline	0
N-Methylaniline	0
Diphenylamine	Trace
Quinoline	0
Pyridine	0
Triethylamine	0

* 3.0×10^{-2} mol./l. of each amine and *p*-tolyl methyl sulfone were used.

was present in the para position of dimethylaniline, no polymerization occurred even after 3 hr. The nature of the effects of dimethylaniline will be discussed in future.

Copolymerization of styrene and methyl methacrylate with this initiating system has been examined. To an equimolar mixture of styrene and methyl methacrylate 3.0×10^{-2} mol./l. of each of *p*-tolyl methyl sulfone and dimethylaniline were added, and the polymerization was carried out in air at 70°C for 2 hr. A portion (5.7% by weight) of the copolymer was obtained. *Analysis* found: C, 76.09 and H, 8.13%, calculated for the copolymer in the molar ratio of 1:1, $(C_{13}H_{16}O_2)_n$: C, 76.47 and H, 7.84%, respectively. It was evident that a copolymer containing styrene and methyl methacrylate in a molar ratio of approximately 1:1 was obtained.

Experimental results mentioned above suggest that the polymerization is initiated by a combined action of *p*-tolyl methyl sulfone, dimethylaniline, and oxygen. The facts that the polymerization is inhibited with hydroquinone, and a copolymer in a molar ratio of 1:1 is formed from styrene and methyl methacrylate indicate that the polymerization proceeds through a free radical mechanism[5]. So, it is probable that radicals to initiate the polymerization are produced from *p*-tolyl methyl sulfone, dimethylaniline and oxygen, though the details of the reaction forming the radical are not made clear at present.

Experimental

p-Tolyl methyl sulfone was prepared from sodium *p*-toluenesulfinate and methyl iodide in aqueous methanol[1]. The crude product was carefully washed with 10% aqueous solution of sodium carbonate and distilled water, then recrystallized from ethanol, m. p. 87°C. Purification of methyl methacrylate, dimethylaniline, and hydroquinone were given in a previous paper[6]. Styrene was washed with 10% aqueous solution of sodium hydroxide and pure water, dried over anhydrous sodium sulfate and carefully distilled under a reduced pressure in nitrogen through a fractionating column, b. p. 46°C/20 mmHg. Amines were distilled under reduced pressure of 3 mmHg, or recrystallized from ethanol.

Polymerization was carried out in open test tubes as mentioned in the preceding paper[4]. The procedures of the polymerization and the determination of per cent conversions have been reported in a previous paper[6].

Summary

The polymerization of methyl methacrylate is initiated by a combined action of *p*-tolyl methyl sulfone, dimethylaniline, and oxygen. The efficiency of the initiating system is increased by using dimethylanilines substituted with electron-donating groups in the para position. The fact that the 1:1 copolymer of styrene and methyl methacrylate is formed by means of this initiating system suggests the formation of radicals to initiate the polymerization from the initiating system.

The present author wishes to express his thanks to Professor Osamu Simamura of the University of Tokyo for his interest and also Mr. Tsurahide Cho, the President of Tama Kagaku Kogyo Co., for permission to publish this work.

Tama Kagaku Kogyo Co.
2-28 Minamirokugo,
Ota-ku, Tokyo

5) C. Walling, E. R. Briggs, W. Cummings and F. R. Mayo, *J. Am. Chem. Soc.*, **72**, 48 (1950).

6) R. Uehara, This Bulletin, **31**, 685 (1958).

Polymerization of Methyl Methacrylate Initiated by a Combined Action of Di-p-tolylsulfonylhydroxylamine and Oxygen in Air

By Ryoichi UEHARA

(Received January 13, 1959)

Di-*p*-tolylsulfonylhydroxylamine was first prepared by Koenigs[1] through the reaction of nitrous acid on *p*-toluenesulfinic acid:

$$2CH_3C_6H_4SO_2H + HNO_2 = H_2O + (CH_3C_6H_4SO_2)_2NOH$$

It has been found by the present author that di-*p*-tolylsulfonylhydroxylamine initiates the polymerization of methyl methacrylate by a combined action with oxygen in air, and this effect is accelerated by the addition of dimethylaniline[2]. Although some compounds related to di-*p*-tolylsulfonylhydroxylamine such as *p*-toluenesulfinic acid[3] and di-*p*-tolylsulfonylmethylamine[4] are noted as components of the initiating system for the polymerization of methyl methacrylate, nothing has been reported up to the present about the effect of di-*p*-tolylsulfonylhydroxylamine for the polymerization.

In the present paper, experimental results concerning the polymerization of methyl methacrylate intiated by the combined action of di-*p*-tolylsulfonylhydroxylamine and oxygen in air, with or without dimethylaniline, are given.

Fig. 1 shows the per cent conversion versus time of the bulk polymerization of methyl methacrylate in air. The polymerization proceeded at a moderate rate by means of 1.86×10^{-2} mol./l. of di-*p*-tolylsulfonylhydroxylamine (DTSH) alone. By the addition of 2.0×10^{-2} mol./l. of dimethylaniline (DMA) the polymerization proceeded fairly rapidly. 3.1×10^{-2} mol./l. of hydroquinone (HQ) retarded the polymerization initiated with 1.86×10^{-2} mol./l. of di-*p*-tolylsulfonylhydroxylamine, i.e., the rate of polymerization was not affected until the conversion reached approximately 5%, but after that the reaction hardly proceeded at all. In the atmosphere of nitrogen, the polymerization occured with difficulty by means of di-*p*-tolylsulfonylhydroxylamine and dimethylaniline. So, it is evident that oxygen is necessary for the initiation of the polymerization.

Copolymerization of methyl methacrylate

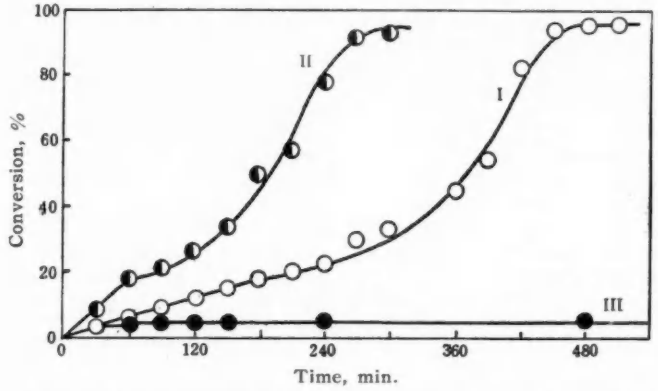


Fig. 1. Per cent conversion versus time of bulk polymerization of methyl methacrylate at 70°C in air. I. DTSH 1.86×10^{-2} mol./l., II. DTSH 1.86×10^{-2} and DMA 2.0×10^{-2} mol./l., III. DTSH 1.86×10^{-2} and HQ 3.1×10^{-2} mol./l.

1) P. Koenigs, *Ber.*, **11**, 616 (1878).
2) R. Uehara, *J. Japan. Chem.* (*Kagaku-no-Ryoiki*), **7**, 291 (1953).
3) For example, H. Bredereck et al., *Ber.*, **89**, 731 (1956).
4) H. Bredereck et. al., *Makromol. Chem.*, **12**, 100 (1954).

and styrene was examined by the initiating system of di-*p*-tolylsulfonylhydroxylamine, oxygen and dimethylaniline. An equimolar mixture of methyl methacrylate and styrene containing 1.7×10^{-2} mol./l. each of di-*p*-tolylsulfonylhydroxylamine and dimethylaniline was heated at 70°C in air. After 2 hr., 9.1% by weight of the copolymer was obtained. Analysis of the copolymer shows that a copolymer in the molar ratio of 1 : 1 has been formed; i. e., found: C, 76.31 and H, 8.03%, calculated for the copolymer in the molar ratio of 1 : 1, $(C_{13}H_{16}O_2)_n$: C, 76.47 and H, 7.84%, respectively. This fact indicates that the polymerization proceeds through a free radical mechanism[5].

Average degrees of polymerization of polymethyl methacrylate formed by means of the initiating system are shown in Table I. In a course of the bulk polymerization by means of 1.86×10^{-2} mol./l. of di-*p*-tolylsulfonylhydroxylamine, the average degrees were approximately constant until the conversion reached 20% (after about 240 min.), while, after that period, they increased gradually corresponding to the extent of the polymerization. Fig. 2 shows the correlation of the average degree of polymerization of

TABLE I. AVERAGE DEGREE OF POLYMERIZATION, $\overline{P}$, OF POLYMETHYL METHACRYLATE FORMED BY MEANS OF DTSH AT 70°C IN AIR

DTSH (mol./l.$\times10^2$)	Time (min.)	Conversion (%)	$\overline{P}$
1.86	30	3.1	2280
〃	60	6.1	2540
〃	90	9.8	2570
〃	120	13.0	2580
〃	240	23.1	2880
〃	300	33.5	3820
〃	360	45.1	3910
〃	420	79.6	3940
〃	480	95.8	3990
〃*	60	16.2	1310
〃*	120	26.8	1560
〃*	180	49.5	1830
3.13	30	4.5	1760
4.50	〃	4.8	1490
5.12	〃	5.0	1310
6.30	〃	6.0	1280
7.19	〃	6.3	1110
8.20	〃	6.5	1080
9.00	〃	6.6	940

* With an equimolar amount of dimethylaniline.

5) C. Walling, F. R. Briggs, W. Cummings and F. R. Mayo, *J. Am. Chem. Soc.*, 72, 48 (1950).

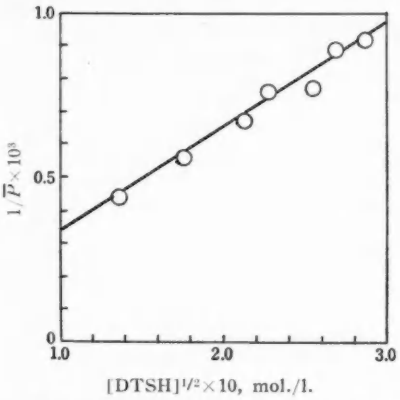
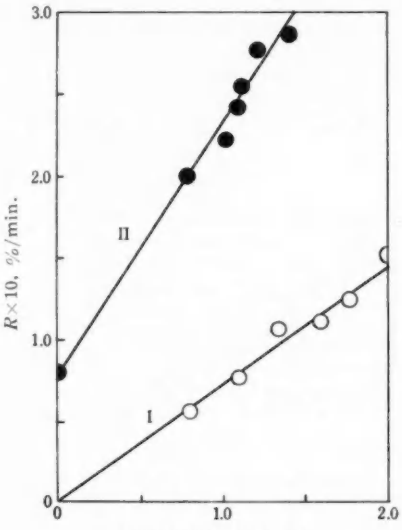


Fig. 2. Correlation of the average degree of polymerization of polymethyl methacrylate with the initial concentration of DTSH at 70°C in air.

polymethyl methacrylate formed during the course of the first 30 min. of the polymerization with the initial concentration of di-*p*-tolylsulfonylhydroxylamine. It is seen that the reciprocal of the average degree of polymerization is linearly dependent upon the square root of the intial concentration of di-*p*-tolylsulfonylhydroxylamine. This fact also indicates the radical character of the polymerization.

The relation between the initial rate of polymerization and concentrations of di-*p*-tolylsulfonylhydroxylamine and dimethylaniline has been investigated. The correlation of the initial rate of polymerization in air with the concentration of di-*p*-tolylsulfonylhydroxylamine is shown in Fig. 3 by line I. The initial rate of polymerization is linearly proportional to the square root of the initial concentration of di-*p*-tolylsulfonylhydroxylamine. When the concentration of di-*p*-tolylsulfonylhydroxylamine was kept constant and various amounts of dimethylaniline were added, the initial rate of polymerization was linearly dependent upon the square root of the initial concentration of dimethylaniline. Line II in Fig. 3 shows this relation in a case when 1.2×10^{-2} mol./l. of di-*p*-tolylsulfonylhydroxylamine was used. It is evident that the so-called square root dependence which is typically seen in the radical polymerization of vinyl monomers holds between the initial rate of polymerization and the initial concentration of both di-*p*-tolylsulfonylhydroxylamine and dimethylaniline. This fact can be regarded as supporting the



$[DTSH]^{1/2}\times10$ for I
$[DMA]^{1/2}\times10$ (with 1.20×10^{-2} of DTSH) for II
mol./l.

Fig. 3. Correlations of the initial rate of polymerization with concentrations of DTSH and DMA at 70°C in air.

radical character of the polymerization reaction.

The accelerating effect of dimethylanilne is significantly influenced by groups substituted in its para position. The per cent conversions of the polymerization after 1 hr. at 70°C accelerated by using various amines are compared in Table II. Electron-donating groups such as methyl and methoxy promote, and electron-withdrawing groups such as chloro and bromo reduce the efficiency of the initiating system. By strongly electron-withdrawing groups such as nitro and nitroso, the polymerization-initiating action of the initiating system is completely lost.

TABLE II. EFFECTS OF *p*-SUBSTITUTED DIMETHYLANILINE ON THE EFFICIENCY OF THE INITIATING SYSTEM

Substituted group	% Conversion after 1 hr.
CH_3O	30.4
CH_3	23.5
H	16.0
Cl	8.1
Br	7.3
NO	0
NO_2	0

Di-*p*-tolylsulfonylhydroxylamine (1.86×10^{-2} mol./l.) and the amine (2.0×10^{-2} mol./l.) were used at 70°C in air.

From the above mentioned experimental results, it is evident that the polymerization of methyl methacrylate initiated by a combined action of di-*p*-tolylsulfonylhydroxylamine and oxygen, with or without dimethylaniline as an accelerator, proceeds through a free radical mechanism. Therefore, it is very probable that a radical to initiate the polymerization is produced from the initiating system, though the nature of the initiating reactions will be the subject of further investigations.

Experimental

Purification of methyl methacrylate, dimethylaniline, and hydroquinone have been reported in a previous paper by the present author[6]. Di-*p*-tolylsulfonylhydroxylamine was prepared from sodium *p*-toluenesulfinate, sodium nitrite, and hydrochloric acid at 0°C[1]. The crude product was washed with distilled water until no ions of chloride and heavy metals were detected in the washing to eliminate water soluble impurities, and recrystallized from benzene and methanol, m. p. 127°C, with decomposition.

Polymerizations were carried out in open test tubes which have been mentioned in a previous paper by the author[7]. Di-*p*-tolylsulfonylhydroxylamine and dimethylaniline were dissolved in methyl methacrylate cooled in an ice-salt bath. The solution (2 cc.) was placed in each of the tubes and heated in a thermostat bath with shaking. The procedures of the polymerization and determination of the initial rate of polymerization have been given previously[6]. The initial rate was expressed in unit of per cent per minute. The average degree of polymethyl methacrylate was estimated from its intrinsic viscosity in chloroform by using the equation of Sakurada[8].

Summary

The polymerization of methyl methacrylate is initiated by a combined action of di-*p*-tolylsulfonylhydroxylamine and oxygen. The polymerization is accelerated with dimethylaniline and retarded with hydroquinone. The initial rate of polymerization is linearly dependent upon the square roots of concentrations of di-*p*-tolylsulfonylhydroxylamine and dimethylaniline in air. The reciprocal of the average degree of polymerization of the

6) R. Uehara, This Bulletin, **31**, 685 (1958).
7) R. Uehara, This Bulletin **32**, 1079 (1959).
8) I. Sakurada, *Chem. High Polymers* (*Kobunshi Kagaku*), **2**, 253 (1945).

polymethyl methacrylate formed by means of the present initiating system is proportional to the square root of the initial concentration of di-*p*-tolylsulfonylhydroxylamine. A copolymer (1 : 1) is obtained from an equimolar mixture of styrene and methyl methacrylate. These facts suggest that the polymerization is initiated by a radical produced from the initiating system.

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Tama Kagaku Kogyo Co.
2-28 Minamirokugo
Ota-ku, Tokyo

On the Phase Transition of Hexamethyldisilane

By Hiroshi SUGA* and Syûzô SEKI

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So-called plastic crystal was first defined by Timmermans[1] in 1938 as a class of crystals which have the entropy of fusion less than about 5 e. u., being miscible together regardless of the difference in the molecular shape, and show much larger plastic flow than the ordinary crystals. This kind of crystal usually undergoes phase transition with much larger entropy change than that at the melting point and the phase just below the melting point possesses a peculiar nature such as that mentioned above. Since then, a number of crystals were found to belong to this category. In general, most of these crystals were composed of more or less globular molecules and these molecules having methyl or methylene groups at the molecular peripheries are the typical case ; i. e., $C(CH_3)_4$[2], $C(SCH_3)_4$[3], cyclohexane[4], $Be_4O(CH_3COO)_6$[5], camphor[6], etc. These kinds of molecules in the lattice are considered to be held together mainly by the weak van der Waals force in respect of the rather small heat of sublimation, and the molecules are characterized by the violent thermal motions such as statistical randomness of molecular orientation or, moreover, by such a factor as self-diffusion which was revealed by recent investigations with nuclear magnetic resonance absorption[7] or in other ways.

In the previous paper[8], the present authors and others have reported the results of preliminary investigations of the phase transition of hexamethyldisilane by thermal and X-ray methods and found that this material really belongs to the category of the plastic crystal. We have also published already the result of the investigation by use of the nuclear magnetic resonance method on the present crystal[9]. So, in the present paper we should like to confine ourselves to reporting mainly the results obtained by the thermal method.

Experimental

Material.—The hexamethyldisilane used in this investigation was prepared by the courtesy of Dr. Nozakura from hexachlorodisilane and the methyl Grignard reagent[10] and purified by

* Present address: Department of Physics, Osaka University, Nakanoshima, Osaka.

1) J. Timmermans, *J. chim. phys.*, **35**, 331 (1938).

2) J. G. Aston and G. H. Messerly, *J. Am. Chem. Soc.*, **58**, 2354 (1936); J. G. Powles and H. S. Gutowsky, *J. Chem. Phys.*, **21**, 1695 (1953).

3) H. J. Backer and W. G. Perdok, *Rec. trav. chim.*, **61**, 533 (1943); W. G. Perdok and P. Terpstra, ibid., **62**, 687 (1943); **65**, 493 (1946).

4) J. G. Aston, G. J. Szasz and H. L. Fink, *J. Am. Chem. Soc.*, **65**, 1135 (1943); E. R. Andrew and R. G. Eades, *Proc. Roy. Soc.* (*London*), **A216**, 398 (1953).

5) T. Watanabé, Y. Saito, *Nature*, **163**, 225 (1949); T. Watanabé, Y. Saito and H. Koyama, ibid., **164**, 1056 (1949); M. Momotani, S. Seki, H. Chihara and H. Suga, This Bulletin, **28**, 325 (1955).

6) A. H. White and S. O. Morgan, *J. Am. Chem. Soc.*, **57**, 2078 (1935); K. Schäfer and O. Frey, *Z. Elektrochem.*, **56**, 882 (1953).

7) E. R. Andrews, "Nuclear Magnetic Resonance", Cambridge Univ. Press, Cambridge (1955).

8) H. Suga, S. Seki, Y. Chatani and I. Taguchi, *Ann. Report Inst. Fiber Res.* (Osaka Univ.), **8**, 51 (1954), (in Japanese); Y. Chatani, H. Suga and I. Taguchi, Annual Meeting of the Chemical Society of Japan, held at Tokyo, April, 1955.

9) T. Yukitoshi, H. Suga, S. Seki and J. Itoh, *J. Phys. Soc. Japan*, **12**, 506 (1957).

10) W. C. Schumb and C. M. Saffer, Jr., *J. Am. Chem. Soc.*, **61**, 363 (1939).

fractional distillation under ordinary pressure, b.p. 112.8~113.0°C. After repeated fractional crystallizations, the sample obtained was finally purified by vacuum distillation, m. p. 14.2~14.4°C. It has been found in the course of purification that this crystal showed remarkably the so-called "vapor snake" phenomenon[11] which seemed to be characteristic of the crystal having low heat of fusion and high triple-point pressure.

Procedure and Apparatus.—For the reaffirmation of the occurrence of the phase transition, the method of the differential thermal analysis (DTA) was employed by using alumina powder as a reference substance. The sample was distilled into a DTA test tube and then sealed off in vacuo. After cooling down to the liquid nitrogen temperature, the sample was heated at a nearly constant rate 0.75°C/min. The apparatus was similar to that[12] used hitherto in our laboratory except for the automatic controller device for the constant heating rate with the reference substance and also the automatic recording of the temperature difference between the sample and the reference substance. The details of the automatic controller and recorder will be reported elsewhere in the near future. In order to determine the accurate temperatures and enthalpy changes associated with the polymorphic transition and fusion, respectively, the heat capacity was determined over the temperature range from −80 to +40°C with the conduction calorimeter which was the same one[13] used in our laboratory with a slight modification. The sample-containing cell was made anew of eighteen-carat gold plate with a wall thickness of 0.03 cm. and was approximately 2.5 cm. in height and 1.5 cm. in diameter. Eight radial fines of thin platinum sheet were silver-soldered inside the calorimeter to aid in establishing good heat distribution. In order to ensure thermal equilibrium, the heating rate employed was 0.25~0.30°C/min. except for around the transition and fusion points where a much slower heating rate was necessary. The vapor pressure measurements were carried out below and above the melting point of this crystal by using a simple glass-made mercury manometer with a sufficiently degassed sample.

Results and Discussion

Fig. 1. gives the result of the differential thermal analysis. The heat effect accompanied by the phase transition (at about −52°C) was three times as large as that corresponding to the fusion and consistent with the previous preliminary result[8]. The high temperature phase looks uniformly transparent, to a glassy mass, and always accompanies the vapor snake phenomenon as far as the air is absent. The microscopic observation indicates that this phase is optically isotropic. On cooling this phase, it is observed to be converted into a polycrystalline, opaque mass at the transition point where the appearance of the birefringence was observed under the microscopic observation.

The heat capacity data are tabulated in Table I and their variation with temperature is plotted in Fig. 2. Table II gives enthalpy and entropy changes accompanying the transition and fusion processes, respectively. In order to determine the true melting point of hexamethyldisilane and also to test the amout of impurity

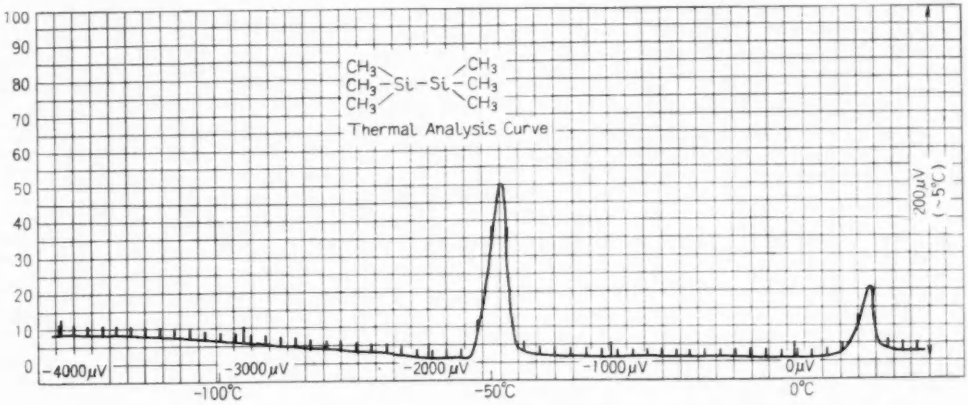

Fig. 1. Automatic recording curve of the differential thermal analysis for hexamethyldisilane.

11) S. Seki, *Science [Japan]* (*Kagaku*), **18**, 277 (1948); M. K. Phibbs and H. I. Schiff, *J. Chem. Phys.*, **17**, 843 (1949); F. C. Frank, ibid., **18**, 231 (1950); S. Seki, ibid., **18**, 397 (1950); R. Verschingel and H. I. Schiff, ibid., **22**, 723 (1954).

12) H. Chihara and S. Seki, This Bulletin, **26**, 88 (1953).

13) I. Nitta, S. Seki and M. Momotani, *Proc. Japan Acad.*, **26**-9, 25 (1950); S. Seki, M. Momotani, K. Nakatsu and T. Ōshima, This Bulletin, **28**, 411 (1955).

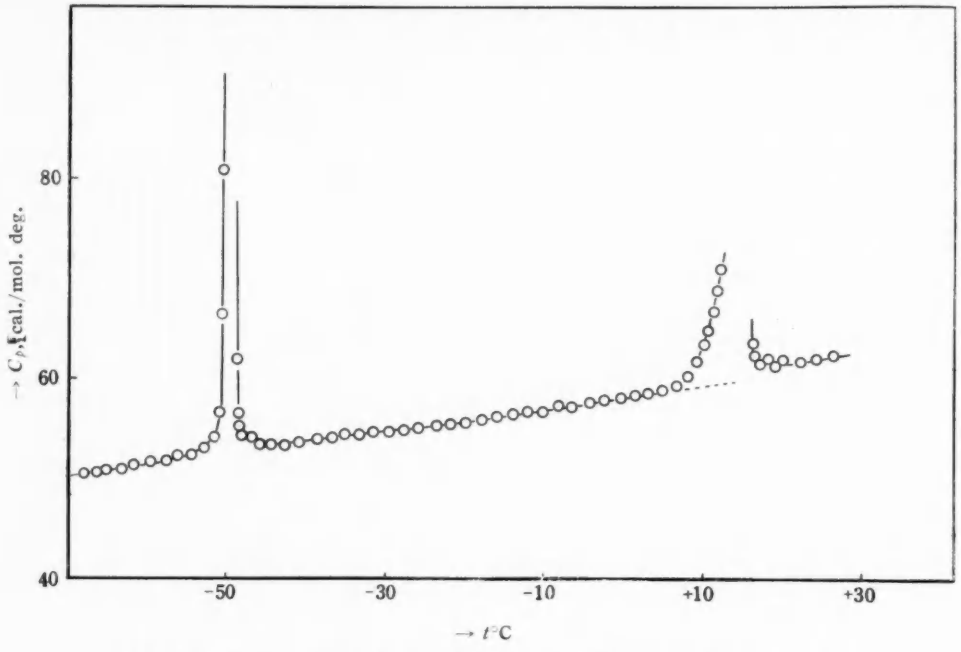

Fig. 2. Heat capacity of hexamethyldisilane as a function of temperature.

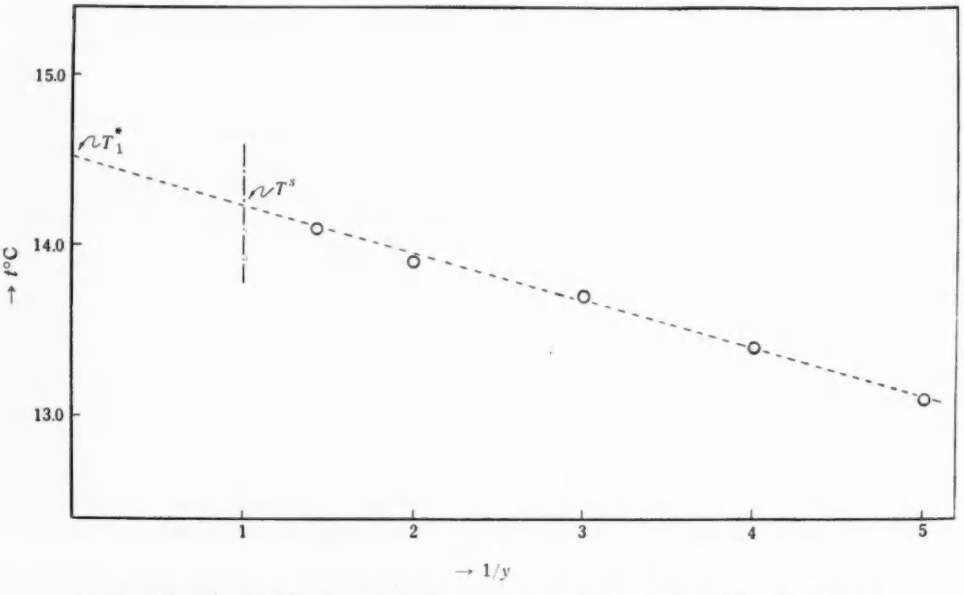

Fig. 3. Plot of the temperature of the liquid-solid equilibrium for hexamethyldisilane as a function of the reciprocal of the fraction of sample melted. T^s is the m.p. of the actual sample, and T_1^* is the m.p. of an absolutely pure sample.

Table I. C_p of hexamethyldisilane as a function of temperature

t°C	C_p (cal./mol. deg.)	t°C	C_p (cal./mol. deg.)
−66.96	50.76	−21.36	55.10
−63.42	50.46	−18.13	55.08
−61.21	51.40	−12.76	55.45
−57.18	52.21	−10.07	55.58
−55.30	52.27	− 7.59	55.69
−54.39	52.66	− 4.41	56.26
−53.49	53.33	− 1.21	56.64
−52.87	53.77	2.91	58.12
−52.58	62.16	5.28	61.45
— transition —		8.42	66.68
−49.37	74.67	11.39	96.30
−48.13	53.88	12.55	141.32
−47.39	52.96	— fusion —	
−44.70	53.49	16.71	60.19
−41.11	53.61	17.70	61.41
−38.20	53.79	19.22	60.84
−34.39	53.74	21.78	61.44
−30.09	54.27	22.52	61.16
−26.23	54.64		

Table II. Temperatures, enthalpies and entropies of transition and fusion of hexamethyldisilane

	T°K	ΔH (cal./mol.)	ΔS(e. u.)
Transition	221.8	2330	10.5
Fusion	287.7$_2$	721	2.51

involved in the used sample, the well-known thermodynamic equation[14]

$$T = T_1^* - (\boldsymbol{R}T_1^{*2}/\Delta H_f)(N/y)$$

was used. Here, T and T_1^* are the apparent and true melting points of the material, respectively; $\boldsymbol{R}$, gas constant; ΔH_f, the enthalpy of fusion; N, the number of moles of impurity; and y, the number of moles of material melted. Fig. 3 represents a plot of equilibrium temperatures against the various amounts melted. As is shown, the observed T versus $1/y$ relationship gives a straight line whose slope makes it possible to determine the value of N, by using the measured value of ΔH_f. As the result, we have determined the true melting point of hexamethyldisilane to be 14.5$_6$°C and the purity of the sample was 99.87% pure (the m. p. reported in the literature is 14.0~14.4°C[15]).

Table III gives the vapor pressure data of the liquid and solid states. The observed values in the liquid range are in good agreement with those of Brockway and Davidson[15]. By applying the method of least squares, good linear relations are obtained between $\log P$ and $1/T$ in both phases. The table also includes the changes of free energy, enthalpy and entropy accompanying the vaporization and sublimation processes, respectively. As the difference between the heat of vaporization and of sublimation, one can obtain the heat of fusion 697±41 cal./mol. which agrees within their experimental errors with the calorimetric value mentioned above.

Table III. Vapor pressure data of hexamethyldisilane in the solid and liquid states

Solid state		Liquid state	
T°K	P, mmHg	T°K	P, mmHg
274.52	7.648	287.62	16.546
275.27	7.917	289.45	18.286
279.14	10.179	291.87	20.850
280.51	11.075	294.34	23.758
282.04	12.190	296.78	26.884
283.61	13.405	299.32	30.664
284.34	14.867	301.54	34.124
286.56	15.831	303.01	36.830
		304.19	38.940
		307.09	44.853
		310.39	52.037

$\log P = -2105.37/T + 8.550$ (in the solid state)
$\log P = -1953.12/T + 8.011$ (in the liquid state)

	ΔH(cal./mol.)	ΔS (e. u.)	$\Delta G^0_{298.16}$
Sublimation	9640±25	25.96±0.17	1900±76
Vaporization	8943±16	23.49±0.05	1940±32
Fusion	697±41 (obsd. 721)		

Table IV. Entropies of transition and fusion of hexamethyldisilane and also of related compounds available for comparison

	$Si_2(CH_3)_6$[a)]	Si_2F_6[b)]	$C_2(CH_3)_6$[c)]	C_2F_6[d)]	C_2Cl_6[c)]
ΔS_{tr}	10.5	—	3.13	8.59	1.93 5.70
ΔS_f	2.51	13.8	4.82	3.71	5.50
ΔS_{total}	13.0	13.8	8.0	12.3	13.1

a) Present study.
b) The values were quoted from F. D. Rossini et al., "Selected values of Chemical Thermodynamic Properties", U.S. Government Printing Office, Washington (1952).
c) D. W. Scott and H. M. Huffman, *J. Am. Chem. Soc.*, **74**, 883 (1952). Recent dilatometric observation revealed another instance of polymorphism near the m. p. [W. F. Seyer, R. B. Sennet and F. C. Williams, *J. Am. Chem. Soc.*, **71**, 3447 (1949)].
d) S. Seki and M. Momotani, This Bulletin, **23**, 30 (1950).

14) For example, S. Seki, *Japan Analyst* (*Bunseki Kagaku*), **6**, 737 (1957).
15) L. O. Brockway and N. R. Davidson, *J. Am. Chem. Soc.*, **63**, 3287 (1941).

of the transition and of the fusion of the present substance together with those of the related compounds. As is evident for all compounds except for C_2Me_6, the sum of both entropies of the transition and fusion is nearly equal to 13.0 e. u., the value predicted from the Walden rule[16], which holds for the entropy of fusion of usual organic compounds. Accordingly, the transition phenomenon of these compounds may be reckoned as the beginning of the melting process. In other words, the total amount of entropy change which ordinarily should be gained at the melting point is divided between the transition and the melting processes. In the case of hexamethyldisilane, the observed entropy of fusion is very close to the value 2.0 e. u. calculated theoretically for a communal entropy of fusion[17], which comes from the communal sharing of free volume in the liquid state. Considering the reverse (freezing) process, it may be reasonable to infer that the liquid of hexamethyldisilane freezes only with respect to the translational motion** of the molecule at the freezing point and does not do so with respect to the rotational or orientational motion until the transition point is reached. And, even at the transition point, it seems that the stopping of the rotational motion of the methyl group about the Si–C axis does not take place yet. This is because the sum of the entropies of fusion and of transition for hexamethyldisilane is almost equal to that for hexachlorodisilane which is isoelectronic with the former and possesses no corresponding rotational group. This thermodynamical conclusion coincides with the result obtained from the nuclear magnetic resonance experiment[9] which revealed that the rotational motion of the methyl group about the Si–C axis was already excited even at temperatures far below the transition point.

In the X-ray investigation[8] of hexamethyldisilane, it was found that the high temperature phase belongs to body-centered cubic lattice with the cell constant of 8.47Å (at 0°C) containing two molecular units and that the molecular axis (Si–Si axis) is orientated randomly among the four body-diagonals. The observed reflection lines were also interpreted semi-quantitatively by assuming a D'_{3h} model (internal free rotation about the Si–Si axis), or alternatively assuming either a D_{3d} or a D_{3h} model combined with overall rotation of the molecule about the molecular axis, by using the value 18 for the temperature factor in all cases. On the other hand, the crystal structure of the low temperature phase was not yet determined, owing to the difficulty of preparing a single crystal available for the X-ray analysis (it may be hexagonal or orthorhombic crystal system[8]). The anomalously large value of the temperature factor in the high temperature phase is qualitatively in accordance with the large value of the entropy of transition. In passing it may be added here that the studies of Raman and infrared spectra[18] of hexamethyldisilane revealed that the molecule in the liquid state has a D_{3h} or a D'_{3h} equilibrium configuration, excluding a D_{3d}-type.

Now, we shall infer from the entropy consideration what sorts of molecular motions will be excited on passing through the transition point from the ordered low-temperature phase to the plastic crystal phase. Referring to the results of X-ray and spectroscopic investigations mentioned above, the following model may be assumed reasonably. In the high temperature phase, the molecular orientation (motion 1) is randomly distributed among the four body-diagonals and the two kinds of internal rotation (motion 2, about Si–Si axis ; motion 3, about Si–C axis) combined with the overall molecular rotation about the molecular axis (motion 4) are fully excited, whereas the motions are highly hindered except for motion 3 in the low temperature phase though not so below the transition point[9]. Then each contribution from the enhancement of such a kind of motion to the entropy of transition can be estimated in terms of statistical mechanics. The contribution from the increase of the orientational freedom (motion 1) is $\boldsymbol{R}\ln 4$ which amounts to 2.54 e. u. The contribution from motion 2 is calculable by use of Pitzer's table[19], assuming the symmetry number 3 and the potential barrier hindering the internal rotation in the low temperature phase 5.7 kcal./mol.[9] In this case, the moment of inertia is computed

** It may be noted that even in the plastic crystal phase a kind of self-diffusion process seems to occur (see Ref. 9).

16) P. Walden, *Z. Elektrochem.*, **14**, 763 (1908).

17) H. Eyring and J. Hirschfelder, *J. Phys. Chem.*, **41**, 249 (1937).

18) C. C. Cerato, J. L. Lauer and H. C. Beachell, *J. Chem. Phys.*, **22**, 1 (1954). H. Murata and S. Kumada, ibid., **21**, 945 (1953); H. Murata and K. Shimizu, ibid., **25**, 1968 (1955).

19) K. S. Pitzer, *J. Chem. Phys.*, **5**, 469 (1937); K. S. Pitzer and W. D. Gwinn, ibid., **10**, 428 (1942).

using tetrahedral angle for ∠Si–Si–C and the interatomic distance of Si–C, 1.88 Å[20], and also assuming that the three rotating hydrogen atoms in methyl group lie at the position of the carbon atom. This contribution amounts approximately to 2.58 e. u. The sum of both entropies, 5.1 e. u., is only half of the observed entropy of transition, 10.5 e. u., so the remaining contribution from motion 4 seems to amount to nearly equal magnitude. Although the precise estimation of the latter is difficult at the present stage owing to the lack of knowledge about the crystal structure of the low temperature phase and also about the heights of the potential barrier hindering this motion in both phases, we assume tentatively that the rotation is fully excited in the high temperature phase whereas the motion is entirely fixed in the low temperature phase. Then the contribution can be calculated with the following equation

$$\Delta S = R\left[\ln\frac{1}{\pi\sigma}\left(\frac{8\pi^3 I_m kT}{h^2}\right)^{1/2}+\frac{1}{2}\right]$$

where I_m is the moment of inertia about the molecular axis, and σ the symmetry number. The calculated value becomes 5.50 e. u. with the values of $T=222$°K and $\sigma=3$. Thus, the calculated total amount of these three entropies, 10.6 e. u., comes out to be nearly equal to the observed one, 10.5 e.u. Here it may be noticed that we have not completely ignored the overall rotational motions about the other two principal axes, since these motions were partly involved already in motion 1. Probably this fortuitous agreement arises from the situation that the over-estimated entropy value of motion 4 might be canceled by the under-estimaton of motion 1.

In conclusion, we may say that although our discussion on the mechanism of the phase transition in hexamethyldisilane from the point of view of entropy is of semi-quantitative nature, its main feature was explained by combining our thermodynamical study with those of the X-ray crystal analysis and the nuclear magnetic resonance.

20) M. L. Huggins, *J. Am. Chem. Soc.*, **75**, 4123 (1953).

Summary

Measurements of the heat capacity (200～300°K) and the vapor pressure (274～310°K) were carried out covering the transition and melting points of hexamethyldisilane. The following results were obtained; T_{tr} 221.8°K, ΔH(transition) 2330 cal./mol., ΔS(transition) 10.5 e. u.; T_f 287.7$_2$°K, ΔH(fusion) 721 cal./mol., ΔS (fusion) 2.51 e. u.; vapor pressure equations,

$$\log P(\text{mmHg}) = -2105.4/T+8.5503$$
$$(274.5\sim286.6\text{°K})$$
$$\log P(\text{mmHg}) = -1953.1/T+8.0105$$
$$(287.6\sim310.4\text{°K});$$

ΔH_{sub} 9640±25 cal./mol., ΔS_{sub} 26.0±0.17 e.u., $\Delta G°_{298.16}$(sub.) 1900±76 cal./mol.; ΔH_{vap} 8943±16 cal./mol., ΔS_{vap} 23.5±0.05 e. u., $\Delta G°_{298.16}$(vap.) 1940±31 cal./mol.

These data showed that the present crystal belongs to the class of plastic crystal. We have discussed the qualitative nature of the phase transition in the present crystal from the point of view of entropy, referring to the X-ray and the nuclear magnetic resonance studies. The remarkable "vapor snake" phenomenon was also observed on this material.

In conclusion, the authors wish to express their sincere thanks to Professor I. Nitta for his valuable advice and continued interest in the present study. The cost of this research has been defrayed from the Scientific Research Encouragement Grant from the Ministry of Education to which the authors' thanks are due.

Department of Chemistry
Faculty of Science
Osaka University
Nakanoshima, Osaka

*Stereoregular Polymers. I. Polymerization of Styrene by Triethylaluminum-Titanium Tetrachloride Catalysts**

By Shunsuke MURAHASHI, Shun'ichi NOZAKURA, Masao SUMI and Kōichi HATADA

(Received November 17, 1958)

Much information is now accumulating in regard to the isotactic polymerization of α-olefins. In particular, the reports of Natta and his collaborators[1] are very instructive about the mechanisms of stereospecific polymerization of propylene. These experiments, however, are mainly based on the heterogeneous catalysts composed of triethylaluminum ($AlEt_3$) and titanium trichloride ($TiCl_3$) (Natta's type). Catalysts derived from $AlEt_3$ and $TiCl_4$ (Ziegler's Type) have not been examined in detail mainly because of their poor reproducibility. Recently, Yamazaki has reported some aspects of polymerization of styrene with this type of catalysts[2].

The authors carried out the polymerization of styrene with the heterogeneous catalysts prepared from $AlEt_3$ and $TiCl_4$, and found that the stereospecificity of the catalysts varied very much with the method of preparation of catalytic mixtures.

The object of the present work is to investigate the relationship between property and stereospecificity of the catalysts.

Results and Discussion

Effect of Preparative Conditions of Triethylaluminum-Titanium Tetrachloride Catalysts upon the Stereospecificities of the Catalysts.— Even in the catalysts of the same ratio of $AlEt_3$ to $TiCl_4$ the stereospecificities of the catalytic mixtures varied intensively according to the method of mixing the two components. Some of the experimental data are listed in Table I.

When $AlEt_3$ and the monomer were charged before the introduction of $TiCl_4$, the stereospecificity was very low, and this is probably due to the cationic polymerization with $TiCl_4$. There was only a small difference between two kinds of catalysts that were prepared under the reverse orders of addition of $AlEt_3$ and $TiCl_4$. A very pronounced effect was observed when the catalysts were prepared with or without stirring. In some cases ultrasonic wave was applied in order to effect an efficient agitation. The catalyst that was prepared without stirring had an appearance of solid mass and was colored orange-brown. Such a catalyst yielded a high stereospecificity. When, on the other hand, the catalyst was prepared under mixing, it was a fine black powder and showed a poor stereospecificity. An explanation for this difference will be given later.

Influence of the Ratio of Triethylaluminum to Titanium Tetrachloride. — Preparation of catalysts and polymerization were carried out under stirring by magnetic stirrer. Yields of the atactic and the isotactic polystyrene polymerized on varying the ratios of $AlEt_3$ to $TiCl_4$ are shown in Fig. 1.

The yield of atactic polystyrene decreased rapidly up to the molar ratio (r) of unity and remained almost constant at

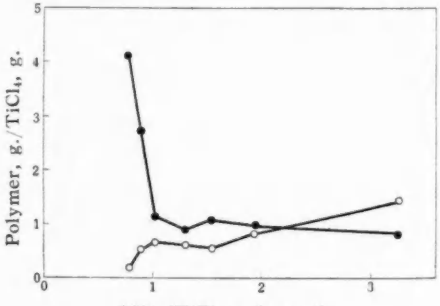

Fig. 1. Polymerization of styrene with Ziegler catalysts.
○ Isotactic polystyrene
● Atactic polystyrene

* Part of this work was presented at the 10th Meeting of the Chemical Society of Japan, Tokyo, April 6, 1957.

1) G. Natta, I. Pasquon and E. Giachetti, *Angew. Chem.*, **69**, 213 (1957); *Makromol. Chem.*, **24**, 258 (1957).

2) N. Yamazaki, *Chem. of High Polymers* (*Kōbunshi Kagaku*), **15**, 49 (1958).

TABLE I. POLYMERIZATION OF STYRENE WITH $AlEt_3$-$TiCl_4$ CATALYSTS PREPARED UNDER VARIOUS CONDITIONS

$TiCl_4$ 0.20 g., *n*-Heptane 15 ml.
$AlEt_3$ 0.36 g., Styrene 5.00 ml.

No.	Preparation of catalysts		Temp., °C	Time, hr.	Conversion, %	Insoluble part in M.E.K., %[c]
	The order of addition	Agitation				
1	Monomer-$AlEt_3$-$TiCl_4$	Stirring[a]	70	4	27.4	23
2	$AlEt_3$-$TiCl_4$-Monomer	Without stirring	70	3	28.0	84
3	〃	Without stirring	15	3	5.2	66
4	〃	Stirring	70	4	15.8	60
5	〃	Stirring and ultrasonic wave[b]	70	4	18.4	39
6	$TiCl_4$-$AlEt_3$-Monomer	Without stirring	70	4	19.5	81
7	〃	Stirring	70	4	7.9	64
8	〃	Stirring and ultrasonic wave[b]	70	4	13.3	4.4

a) Stirring was carried out by a magnetic stirrer.
b) After mixing by a magnetic stirrer, ultrasonic wave (450 KC, ca. 2W./cm^2) was applied for about ten minutes.
c) The percentage fraction of extraction residue with hot methylethylketone in total polymer.

increasing ratios. On the other hand, the yield of isotactic polymer showed a small but gradual increase over the whole range examined.

The high content of atactic polymer that was formed in a condition $r<1$ may reasonably be ascribed to the existence of remaining $TiCl_4$. Furthermore, the appearance of a break on the atactic curve in Fig. 1 seems to indicate the disappearance of $TiCl_4$ and the appearance of another kind of catalyst which also promotes the atactic polymerization of styrene with minor activity, and this kind of catalyst may probably be soluble complex compounds containing titanium and aluminum.

Valency States of Titanium in Catalytic Mixtures.—The reaction between $AlEt_3$ and $TiCl_4$ may be considered to be analogous to that of Grignard's reagent on alkyl orthotitanate[3]. Therefore, the reaction scheme may be written in the following manner:

Alkylation (fast)

$$Et_3Al + TiCl_4 \rightarrow EtTiCl_3 + Et_2AlCl \quad (1)$$

$$Et_3Al + EtTiCl_3 \rightarrow Et_2TiCl_2 + Et_2AlCl \quad (2)$$

Decomposition (slow)

$$EtTiCl_3 \rightarrow Et\cdot + TiCl_3 \quad (3)$$

$$Et_2TiCl_2 \rightarrow 2Et\cdot + TiCl_2 \quad (4)$$

The alkylation reaction may be fast and the decomposition which yields titanium of lower valencies may be comparatively slow.

In order to elucidate the results obtained above, the distribution of the valency states of titanium in catalysts was examined. When $AlEt_3$ and $TiCl_4$ was mixed to produce a heterogeneous catalyst, a gas evolved. According to the gas chromatographic analysis, the gas consisted of a large portion of ethane and small portions of butane and hydrogen. Ethane might be derived from the disproportionation reaction of ethyl radical which occurred in reactions 3 and 4. Ethylene, which is another procuct of disproportionation, was not found. It probably had polymerized in this condition.

On the other hand, the gas, which evolved when the solid catalyst was decomposed by dilute sulfuric acid, was found to be composed mainly of ethane and hydrogen, a small amount of butane, and a trace of ethylene. Ethane might be derived from the hydrolysis of ethyl-metal bond in the catalyst mixture. Hydrogen can be assumed to evolve according to the following reaction[3]:

$$Ti^{2+} + H_2O \rightarrow Ti^{3+} + \frac{1}{2}H_2 + OH^- \quad (5)$$

Therefore, the amount of hydrogen was measured volumetrically by absoption with colloidal palladium and one mole of hydrogen was assumed to be equivalent to two moles of divalent titanium. The total trivalent titanium in the hydrolyzate was then determined by redox titration with ceric sulfate. The results are given in Table II. As expected, the catalyst which was prepared in a condition $r=1$

3) D. F. Herman, W. K. Nelson, *J. Am. Chem. Soc.*, 75, 3877,3882 (1952).

TABLE II. VALENCY STATES OF TITANIUM IN SOLID CATALYSTS

The catalysts were prepared at 70°C in 15 ml. of *n*-heptane from 0.37 g. of $AlEt_3$ and the appropriate amount of $TiCl_4$.

$AlEt_3/TiCl_4$ molar ratio	Preparation of catalyst	Gas evolved		Ti(IV) %	Ti(III) %	Ti(II) %
		When catalyst was prepared, ml.	When catalyst was decomposed, ml.[c]			
1.09	Stirring[a]	41	65	2	98	0
2.44	Stirring[a]	30	116	0	35	65
2.74	Stirring[a]	30	113	0	23	77
2.51	Without stirring[b]	13	133	4	80	16

a) $TiCl_4$ and $AlEt_3$ were added in this order under stirring by a magnetic stirrer.
b) Catalyst components were added in the order of $AlEt_3$ and $TiCl_4$ without stirring.
c) Decomposition was carried out about half an hour after preparation of the catalyst, when evolution of gas had almost entirely ended.

TABLE III. POLYMERIZATION AFTER WASHING THE SOLID CATALYSTS

Styrene (5.00 ml.) was polymerized for 3.0 hr. at 70°C without stirring.

No.	Preparation of catalyst[a]			$AlEt_3$ added after washing, g.	Conversion, %	Insoluble part in M.E.K. %
	$TiCl_4$, g.	$AlEt_3$, g.	Temp., °C			
1	0.44	0.33	70	0.33	28.7	91
2[b]	0.45	0.33	b. p. of *n*-heptane	0.34	33.3	90
3	0.45	0.13	b. p. of xylene[c]	0.33	27.3	92
4	0.40	0.33	b. p. of *n*-heptane	0	79.4	Trace
5	0.23	0.33	b. p. of *n*-heptane	0	45.5	17
6[d]	0.44	0.32 0.32	b. p. of *n*-heptane	Without washing	32.7	86
7[e]	0.44	0.67	70	0.32	2.4	65

a) Generally heterogeneous catalysts were prepared in 15 ml. of *n*-heptane under stirring by a magnetic stirrer. $TiCl_4$ and $AlEt_3$ were added in this order.
b) Polymerization time was 3.2 hr.
c) Xylene wae used as solvent for preparing the catalyst. The catalyst was washed with *n*-heptane as usual, and then the polymerization was carried out in *n*-heptane.
d) $AlEt_3$ (0.32 g.) was added dropwise into the solution of $TiCl_4$ at the boiling temperature of *n*-heptane and the mixture was refluxed for ten minutes and kept for one hour at room temperature, and then the remaining half (0.32 g.) of $AlEt_3$ and monomer was added at 70°C.
e) The order of adding two components was reversed. Into 0.67 g. of $AlEt_3$ was added $TiCl_4$ rapidly under stirring at 70°C and the black, fine precipitate was washed with *n*-heptane and the polymerization was carried out as usual with the secondary addition of $AlEt_3$ and monomer.

contained a small amount of tetravalent titanium, which is responsible for a relatively large amount of atactic polymer. The catalyst, in which r is more than unity, was found to be mainly composed of divalent and trivalent titanium. The reduction of titanium over trivalent state does not seem to have a marked effect upon stereospecificity. In fact, the catalyst that was prepared without agitation, although it included a certain amount of tetravalent titanium and a large amount of trivalent titanium, showed a good stereospecificity and a good catalytic activity.

Influence of Washing the Solid Catalyst.—In order to remove the soluble catalysts which were considered to be responsible for the atactic polymerization, catalyst mixtures were washed with *n*-heptane by decantation and then polymerizations were carried out with or without addition

of further $AlEt_3$. Experimental data are summarized in Table III.

Without the secondary addition of $AlEt_3$ after washing only amorphous polystyrene was obtained, while with its addition the catalyst acquired a very high stereospecificity and also good catalytic activity. However, when $TiCl_4$ was reduced gradually by an equivalent amount of $AlEt_3$ and then an additional equivalent amount of $AlEt_3$ and styrene was added, a good result was obtained (Table III, No. 6).

The catalyst which was prepared by adding $TiCl_4$ to 2.5 times on molar base of $AlEt_3$ under stirring showed a very poor catalytic activity even after washing (Table III, No. 7).

The results seem to suggest the importance of the physical nature of solid catalyst. This subject will be discussed in detail in the later part of this paper.

Recently similar experiments were described in a patent publication where the catalyst was filtered through a glass filter and the effect of filtration was explained there to be due to the removal of the finely dispersed parts of the catalyst[4].

X-ray Study of Solid Catalysts.—The solid catalysts, which were prepared in similar manners to those of Tables I and II, were washed with *n*-heptane and sealed in a small ampoule with a thin wall (Fig. 2), and then exposed to X-ray. It was found in general that the more stereospecific and active catalyst showed the sharper diffraction pattern. X-ray photographs of the catalysts prepared under various conditions are shown in Fig. 3. In the case of the catalyst that was prepared by dropping $TiCl_4$ quickly into the solution

Fig. 2. A capillary ampoule for the X-ray study.

4) S. G. Montecatini and K. Ziegler, Irish Pat., 66,855 (1955).

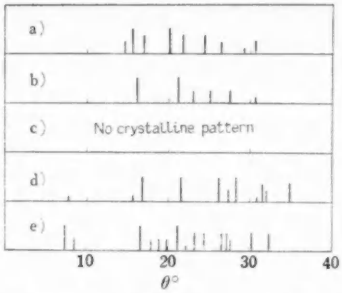

Fig. 3. X-ray powder patterns of catalytic masses (CuKα radiation).
a) $TiCl_4$ (1 mol. equivalent) was added into $AlEt_3$ (2.3 mol. equivalents) at 70°C without agitation.
b) $AlEt_3$ (1 mol. equivalents) was added to $TiCl_4$ 1 mol. equivalent) at 70°C under agitation.
c) $AlEt_3$ (2.3 mol. equivalents) was added quickly into $TiCl_4$ (1 mol. equivalent) at 70°C under agitation.
d) $TiCl_3$, the product of Stauffer Chem. Co.
e) $TiCl_2$[6].

of 2.5 mol. equivalents of $AlEt_3$ at 70°C under agitation, there was found no crystalline reflection but a diffuse halo. Such a catalyst had a poor stereospecificity and catalytic activity.

On the contrary, when either (a) 1 mol. equivalent of $TiCl_4$ was added into 2.4 mol. equivalents of $AlEt_3$ without agitation or (b) 1 mol. equivalent of $AlEt_3$ into the solution of 1 mol. equivalent of $TiCl_4$ under agitation, the solid mass showed moderately crystalline reflections. These reflections are rather diffuse as compared with that of commercial $TiCl_3$, indicating an imperfect growth of the crystals. The reflections coincide with neither that of $TiCl_3$[5] nor that of $TiCl_2$[6]. This fact might suggest the existence of some crystalline complex compound containing Al and Ti or another modification of $TiCl_3$ and $TiCl_2$[7].

The solid mass prepared by method a showed a good stereospecificity and catalytic activity. But in the case of the catalyst b, also good results were obtained

5) W. Klemm and E. Krose, *Z. anorg. u. allgem. Chem.*, **253**, 218 (1947).
6) M. Farber, A. J. Darnell and F. Brown, *J. Chem. Phys.*, **23**, 1556 (1955).
7) F. Böck and L. Moser, *Monatsch.*, **34**, 1825 (1913). The existence of two modifications of $TiCl_3$ was first suggested by Böck and Moser in the study of the heat of solution. Two kinds of $TiCl_3$ were described by them to be violet colored and brown. The violet is the one that is obtaind by reduction of $TiCl_4$ at high temperture and is now available commercially.

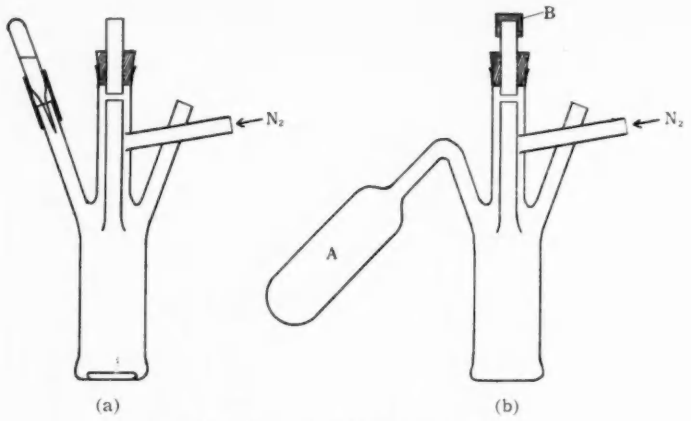

Fig. 4. Vessels for the polymerization.

by washing with *n*-heptane. (Table III, No. 1—3). Although both the catalysts (a and b) gave the crystalline patterns, they showed some differences in details of X-ray diagram. Further study of this point would be necessary, but was not pursued.

Conclusion

Titanium tetrachloride, ethylaluminum chlorides, soluble aluminum-titanium complex compounds, and amorphous insoluble solid are conceivable for the formation of atactic polymer. Titanium tetrachloride is the one that remained unreacted when the molar ratio of $AlEt_3$ to $TiCl_4$ did not exceed unity. The others are considered to be formed by the reaction between $AlEt_3$ and $TiCl_4$. Although the first three can be removed by washing with *n*-heptane, the last one can not.

The content of the crystalline component in solid mass depends upon the condition of reaction between $AlEt_3$ and $TiCl_4$. If the alkylation of $TiCl_4$ proceeded beyond the stage of $EtTiCl_3$ (or Et_2TiCl_2), the sufficient growth of the crystallites of the compound containing $TiCl_3$ (or $TiCl_2$) could not be expected. Moreover, it is a factor to be considered that some amorphous titanium compound would be produced if the alkylation of the unstable compound containing titanium chlorides occurred preferentially before the sufficient growth of crystallites was permitted.

In order to prepare a crystalline catalytic mass, therefore, it is preferable to use $AlEt_3$ in an amount not more than an equivalent of $TiCl_4$. As shown in the experiments, it may be a convenient method for obtaining a crystalline catalytic mass to combine the solutions of two reactants without agitation.

It is noteworthy that the crystalline component of the effective solid catalyst is neither $TiCl_3$ nor $TiCl_2$, and is probably some complex compound containing Al and Ti or the other modification of $TiCl_3$ (or $TiCl_2$). The fact seems to be one of the important differences between catalysts of Ziegler's type (i. e., $AlEt_3$ and $TiCl_4$) and Natta's type (i. e., $AlEt_3$ and $TiCl_3$).

Experimental

Meterials. — Commercial styrene was washed with 10% solution of sodium hydroxide and water, dried over calcium chloride, and distilled in a nitrogen stream before use[8].

n-Heptane was shaken with fuming sulfuric acid, washed with water and dilute alkali, dried over calcium chloride, distilled and stored over sodium chips.

$AlEt_3$ was the product of Mitsui Chem. Ind. Co. and was used as 30% solution in *n*-heptane. Concentration was checked by the amount of ethane evolved when the solution was hydrolyzed.

$TiCl_4$ was the product of Osaka Titanium Co. and used as 21% solution in *n*-heptane. The concentration was checked by determining titanium by redox titration with ceric solution after reduction with zinc amalgam.

Polymerization.—The polymerization vessel is shown in Fig. 4a. *n*-Heptane was placed in the vessel of about 100 ml. capacity and the ampoules of monomer, $TiCl_4$, $AlEt_3$, and a thermometer if necessary were mounted on it through rubber tubings. The air in the apparatus was replaced by dry nitrogen by repeated evacuation and introduction of nitrogen. Then the lower half

8) E. R. Blout and H. Mark, "Monomers", Interscience Publishers, Inc., New York (1949).

of the apparatus was immersed in the thermostat and the contents of the ampoules were dropped in by breaking the top of the ampoule which was previously scratched at the capillar part in order to ease the breaking.

Polymerization was stopped by the introduction of 2 ml. of methanol and 0.3 ml. of concentrated hydrochloric acid and then all the contents were poured onto a large amount of methanol. After standing overnight, the polymer was collected and washed with methanol, and dried.

If the washing of the solid catalyst with *n*-heptane was needed the vessel shown in Fig. 4b was used. The supernatant liquid was decanted into the side flask (A) and 15 ml. of *n*-heptane was injected through a silicone rubber cap (B). The decantation and the injection were repeated three times. The ampoule of $AlEt_3$ now emptied was exchanged with another one in the stream of nitrogen and charged, and then the monomer was dropped in.

Extraction of the Atactic Polymer from the Crude Polymer.—About 0.4 g. of polymer was refluxed with 40 ml. of methylethylketone for several hours. After standing overnight at room temperature, the remaining isotactic polymer was collected, washed with methylethylketone, dried in vacuo at 100°C.

Valency States of Titanium in Catalytic Mixtures.—A gas buret was connected to the reaction vessel of Fig. 4a and an ampoule containing 8 ml. of 10% sulfuric acid was mounted in place of styrene. After the mixing of the catalyst components, 30 to 40 min. was required for almost complete evolution of gas. The reaction vessel was cooled to 0°C and the gas in the vessel was replaced by nitrogen by repeated evacuation and filling. Then the catalyst mixture was hydrolyzed by dropping the aqueous sulfuric acid and the amount of the gas evolved was measured by the gas buret.

An aliquot of the mixed gas was analyzed for hydrogen using colloidal palladium as absorbent.

The hydrolyzed aqueous layer was separated from the organic layer in an atmosphere of carbon dioxide and analyzed for Ti(III) by titration with ceric standard solution using diphenylamine as an indicator. The amount of Ti(III) thus measured was taken as the sum of Ti(II) and Ti(III) in the catalyst mixture. Some of the results are given in Table III.

X-ray Study of Solid Catalyst—The solid catalytic mass was washed with *n*-heptane by decantation, and the slurry of catalyst was brought into a small thin-walled ampoule made of Terex glass (Fig. 2). All the operations were carried out in a nitrogen atmosphere. The ampoule was sealed at A. The solid powder was packed down to the bottom by a centrifuge and exposed to X-ray.

Summary

Styrene was polymerized by the heterogeneous catalysts of Ziegler's type which were prepared under various conditions. The important factors which have pronounced effects on the stereospecificity and the catalytic activity of the mixture are concluded to be the existence of the remaining titanium tetrachloride, ethylaluminum chlorides and some soluble aluminum-titanium complex compounds, and the crystalline nature of the solid catalytic mass. The first three are considered to be responsible for the atactic polymerization of styrene and can be removed by washing with *n*-heptane. The crystallinity of the solid catalyst seems to be necessary for its high stereospecificity and catalytic activity.

The solid catalyst was examined by X-ray. It was found that the crystalline component of the catalyst did not correspond to $TiCl_3$ or $TiCl_2$, and thus it was suggested that some crystalline complex compounds containing Al and Ti or some other modifications of $TiCl_3$ (or $TiCl_2$) would be responsible for the effective catalytic component of Ziegler catalyst. The authors also suggested that the fact might be one of the important differences between the heterogeneous catalysts of Ziegler's type and Natta's type.

The authors wish to thank Mitsui Chem. Ind. Co. for the generous supply of triethylaluminum and Osaka Titanium Co. for titanium tetrachloride. We are also very grateful to Mr. Y. Chatani of Nitta Laboratory who helped us in the experiment of X-ray.

Department of Chemistry
Faculty of Science
Osaka University
Nakanoshima, Osaka

Derivatives of 1,8(9)-p-Menthadien-10-yl-carbinol

By Kyoichi SUGA and Shoji WATANABE

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In the previous paper[1], the preparation of a limonenylcarbinol and the determination of its structure as 1,8(9)-*p*-menthadien-10-yl-carbinol (I) were reported. The present paper describes various derivatives of the limonenylcarbinol.

When a mixture of I and paraformaldehyde was heated at 130~150°C for several hours, a pale yellow viscous oil was obtained. Analysis ($C_{12}H_{20}O_2$) and the molecular weight (192) indicated that the product was an adduct of one mole of formaldehyde to I. The presence of a primary hydroxyl group was proved by a qualitative analysis and an infrared absorption spectrum (9.6 μ). Quantitative acetylation with pyridine and acetic anhydride[2] showed that it was a monohydric alcohol. The infrared absorption spectrum showed characteristic absorption bands of the acetal type at 8.05, 8.6 and 9.0 μ (Fig. 1). From the above results, it was concluded that the structure of the substance is formaldehyde mono-1,8(9)-*p*-menthadien-10-yl-carbinyl acetal (II).

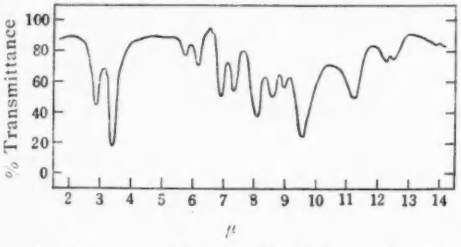


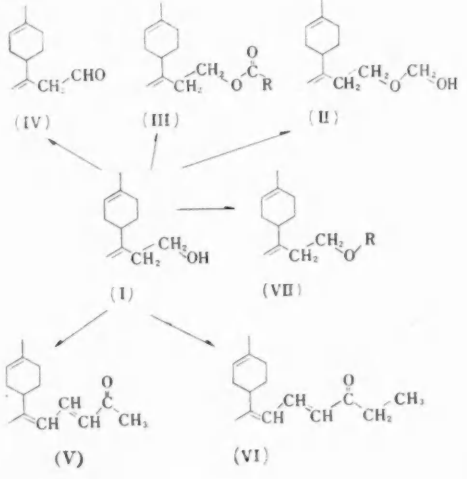
Fig. 1. Infrared absorption spectrum of II.

Various esters (III) were prepared from I. The monoesters of maleic acid, phthalic acid and succinic acid were prepared. The sodium salt of the acid maleate shows remarkable surface activity, and the foaming force is equal to that of the cetylsulfate (Table I). By the action of palmitoyl chloride, capryloyl chloride, isovaleryl chloride, phenylacetyl chloride and cinnamoyl chloride, I gave the esters of the corresponding acids (Table II). The caprylate and the phenylacetate are fragrant.

TABLE I. THE FOAMING FORCE OF SODIUM LIMONENYLCARBINYL MALEATE

%	Numbers of foams after (min.)		Quantities of foams after (min.)	
	2	5	2	5
Na limonenylcarbinyl maleate				
0.50	25.5	13.8	216	184
0.25	19.8	12.3	195	173
0.10	14.0	10.0	114	90
Na laurylsulfate (SO_3: 27.2%)				
0.24	7.4	2.2	857	852
0.15	8.4	2.7	758	753
Na cetylsulfate (SO_3: 22.1%)				
0.30	24.8	16.2	265	256
0.15	19.8	13.4	180	173

By the action of chromic anhydride in glacial acetic acid, a limonenylformaldehyde, 3-(4-methyl-3-cyclohexen-1-yl)-3-buten-1-al (IV) was obtained. Its odor is more fragrant than that of I. It gives positive reactions with Schiff's reagent and Tollen's reagent. The composition was confirmed from those of the 2,4-dinitrophenylhydrazone and semicarbazone.



1) K. Suga, J. Ishii and S. Watanabe, This Bulletin, 32, 711 (1959).

2) N. Sugiyama, "Micro Identification of Organic Compounds (Yukikagobutsu no Biryo Kakuninho)", Baifukan Co, Ltd., Tokyo (1957), p. 60.

TABLE II. MONO-BASIC ACID ESTERS OF THE LIMONENYLCARBINOL

	Refining procedure	Physical constants	Molecular weight Found	Calcd.
Palmitate	Chromatography	n_D^{19} 1.4794	378	404
Caprylate	Chromatography	n_D^{18} 1.4797 $[\alpha]_D^{15}$ +11.7	301	320
Isovalerate	Chromatography	n_D^{19} 1.4884	244	250
Phenylacetate	Vacuum distillation	n_D^{17} 1.5270 b. p. 150C°/4 mmHg $[\alpha]_D^{15}$ +26.0	279	284
Cinnamate	Chromatography	n_D^{11} 1.4822 $[\alpha]_D^{15}$ +15.1	290	296

TABLE III. LIMONENYLCARBINYL ETHERS

	Boiling point °C/mmHg	Refractive index	Specific gravity	Molecular refraction Found	Calcd.	Yield %
Methyl	85~86/12	n_D^{25} 1.4870	$d_4^{24.5}$ 0.9317	55.39	52.61	80
Ethyl	96~97/4~5	n_D^{23} 1.4921	d_4^{23} 0.9353	59.98	59.64	90
Allyl	115~118/17	n_D^{23} 1.4927	$d_4^{24.5}$ 0.9293	64.26	63.79	80
Benzyl	175~179/10	n_D^{23} 1.5300	d_4^{23} 0.9885	80.17	79.13	90

Action of a large excess of acetone and aluminum isopropoxide on I gave a limonenylmethyleneacetone, as a viscous oil with burning odor. The structure of 6-(4-methyl-3-cyclohexen-1-yl)-3,5-heptadien-2-one(V) was demonstrated as follows: The substance gave a 2,4-dinitrophenylhydrazone and a positive iodoform reaction, which showed that it was a methyl ketone. The major absorption peaks at 295 and 223 mμ in the ultraviolet spectrum (Fig. 2) suggested the presence of a conjugated dienone grouping.

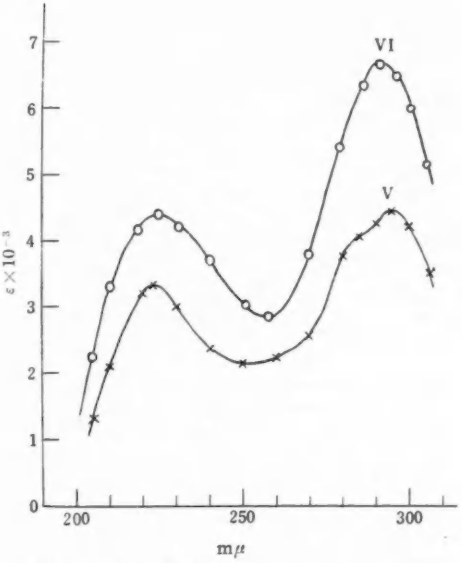


Fig. 2. Ultraviolet absorption spectra of V and VI.

Similarly, 7-(4-methyl-3-cyclohexen-1-yl)-4,6-octadien-3-one(VI) was prepared from I and methyl ethyl ketone. It is more viscous than V and also possesses a burning odor. The composition was confirmed by an elementary analysis of its 2,4-dinitrophenylhydrazone. It showed absorption peaks at 291 and 225 mμ (Fig. 2) corresponding to the conjugated dienone structure(VI). The iodoform reaction was negative.

Some ethers of I were also prepared. I was converted into the sodium compound by the action of sodamide in benzene. The ethyl limonenylcarbinyl ether VII ($R=C_2H_5$) was obtained in a yield of 90% from ethyl bromide and the sodium compound. Its ethoxyl radical was detected by Zeisel's method[3]. Similarly, methyl, ethyl, benzyl and allyl ethers were prepared (Table III).

Experimental

1,8(9)-*p*-Menthadien-10-yl-carbinol(I). — Prepared from *d*-limonene and paraformaldehyde as reported previously[1]: b. p. 102~106°C/4 mm.; d_4^{17} 0.9603; n_D^{17} 1.5020; $[\alpha]_D^{10}$+37.2; phenylurethan, m. p. 56~57°C.

Formaldehyde Mono-1,8(9)-*p*-menthadien-10-yl-carbinyl Acetal.—In a glass tube, 4 g. of I and 0.8 g. of paraformaldehyde were sealed and heated

3) R. L. Shriner, R. C. Fuson and D. Y. Curtin, "The Systematic Identification of Organic Compounds", 4th Ed., John Wiley & Sons, Inc., New York; Maruzen Co., Ltd., Tokyo (1956), p. 116.

at 150~170°C for 6 hr. By fractional distillation, 1.5 g. of II was given: b. p. 155~162°C/5 mm.; $n_D^{20.5}$ 1.5066; $d_4^{20.5}$ 1.0306; molecular refraction 56.64 (calcd. for $C_{11}H_{17}OCH_2OH$: F_2, 57.65); hydroxyl group, 6.03% (calcd. for monohydric alcohol, 8.68%); molecular weight, 192 (calcd. for $C_{12}H_{20}O_2$: 196.2).

Anal. Found: C, 72.17; H, 9.41. Calcd. for $C_{12}H_{20}O_2$: C, 73.40; H, 10.27%.

The Limonenylcarbinyl Monoesters of Dibasic Acids.—*1,8(9)-p-Menthadien-10-yl-carbinyl hydrogen maleate.*—A mixture of 2 g. maleic anhydride and 2 g. of I was heated at 100°C for 3 hr. The reaction mixture was thoroughly washed with water of 60°C, dried in vacuo, and 3 g. of a pale yellow monoester was obtained, n_D^{12} 1.4921. Molecular weight, 264.25[4] (calcd. for $C_{15}H_{20}O_4$: 264.2). The silver salt was prepared by adding silver nitrate solution to the sodium salt of the acid maleate.

Anal. Found: Ag, 29.75; Calcd. for $C_{15}H_{19}O_4Ag$: Ag, 29.08%.

The foaming force of the sodium salt solution was measured by Nakajima's method[5] (Table I).

Acid phthalate and acid succinate of I.—They were prepared similarly.

The Limonenylcarbinyl Esters of Monobasic Acids. — *1, 8(9)-p-Menthadien-10-yl-carbinyl palmitate.*—To a mixture of 1.5 g. of I and 20 cc. of anhydrous ether, a dry ethereal solution of 3.0 g. of palmitoyl chloride was added with stirring. The reaction mixture was left overnight at room temperature. The crude palmitate was extracted with ether and the extract was washed three times with 30% aqueous methanolic solution containing 5% potassium hydroxide, and several times with water, and dried over anhydrous sodium sulfate. The crude palmitate, obtained by evaporation of the solvent, was chromatographed on active alumina and the pale yellow part in the middle of the chromatogram was eluted with methanol. By removing the methanol, 2.0 g. of the palmitate was obtained.

Caprylate, phenylacetate and cinnamate.—They were prepared similarly (Table II).

3-(4-Methyl-3-cyclohexen-1-yl)-3-buten-1-al (IV).—To a mixture of 4 g. of chromic anhydride, 5 cc. of water and 100 cc. of glacial acetic acid, a mixture of 9 g. of I, 30 cc. of acetone and 20 cc. of glacial acetic acid was added in 25 min. at 50~55°C with vigorous agitation, and the mixture was stirred for 4.5 hr. Then this was poured into a large amount of water and extracted with ether. The extracts were washed with water and dried over anhydrous sodium sulfate. By fractional distillation, 3.5 g. of IV was obtained: b. p. 88°C/4 mm.; n_D^3 1.5045. It gave a positive reaction with Schiff's reagent and reduced an ammoniacal silver nitrate solution.

2, 4-Dinitrophenylhydrazone.—It was prepared as usual and recrystallized twice from a mixture of pyridine and methanol. Fine red crystals, m. p. higher than 220°C.

Anal. Found: N, 16.14. Calcd. for $C_{17}H_{20}O_4N_4$: N, 16.27%.

Semicarbazone.—A mixture of IV, semicarbazide hydrochloride, sodium acetate and methanol was allowed to stand for about a month, and the crystals produced were collected and recrystallized twice from methanol. Colorless needles, m. p. 192°C.

Anal. Found: N, 18.35. Calcd. for $C_{12}H_{19}ON_3$: N, 18.98%.

6-(4-Methyl-3-cyclohexen-1-yl)-3, 5-heptadien-2-one (V).—A mixture of 5 g. of I, 18.5 g. of aluminum isopropoxide, 150 g. of refined acetone and 150 g. of anhydrous benzene was refluxed for 40 hr. Then 300 g. of benzene was added to the reaction mixture, and the benzene solution was separated, washed with 30% sulfuric acid three times and with water several times, and dried over anhydrous sodium sulfate. After benzene was evaporated, 1.0 g. of V was obtained by fractional distillation: b. p. 125~133°C/3 mm.; n_D^{10} 1.5271; λ_{max} 295 mμ, ε 4480; λ_{max} 223 mμ, ε 3340. The substance gave a positive iodoform reaction.

2, 4-Dinitrophenylhydrazone.—This was prepared as usual and recrystallized from ethylacetate. Red needles, m. p. 179~180°C.

Anal. Found: N, 14.50. Calcd. for $C_{20}H_{24}O_4N_4$: N, 14.50%.

7-(4-Methyl-3-cyclohexen-1-yl)-4, 6-octadien-3-one (VI).—A mixture of 7 g. of I, 24 g. of aluminum isopropoxide, 200 g. of refined methyl ethyl ketone and 200 g. of dry benzene was refluxed for 60 hr. It was poured into 30% sulfuric acid and extracted with ether. The extracts were washed with water and dried over anhydrous sodium sulfate. By fractional distillation, 2.0g. of VI was obtained: b. p. 125~132°C/2 mm.; n_D^{23} 1.4806; λ_{max} 291 mμ, ε 6650; λ_{max} 225 mμ, ε 4340. It did not give a positive iodoform reaction.

2, 4-Dinitrophenylhydrazone.—This was prepared as usual and recrystallized twice from a mixture of ethyl acetate and ethanol. Red needles, m. p. 203°C.

Anal. Found: N, 14.11. Calcd. for $C_{21}H_{26}N_4O_4$: N, 13.99%.

The Ethers of the Limonenylcarbinol (VII).—*Ethyl 1, 8(9)-p-menthadien-10-yl-carbinyl ether* (R=C_2H_5).—To a benzene solution (100 cc.) of 4.3 g. of sodamide, 12.4 g. of I was added gradually at 60~65°C with vigorous agitation. When ammonia gas was no more generated, 13.3 g. of ethyl bromide was added in drops and the mixture was stirred for three hours. After leaving it overnight, the benzene solution was washed with water, and dried over anhydrous sodium sulfate. By fractional distillation 13.1 g. of VII was given.

Anal. Found: C, 80.04; H, 11.61. Calcd. for $C_{13}H_{22}O$: C, 80.34; H, 11.41%.

The ethoxyl radical was detected by Zeisel's method.

Methyl, benzyl and allyl ethers.—These were prepared similarly.

Absorption Spectra. — Infrared absorption spectra were measured by using a Perkin-Elmer spectrophotometer and ultraviolet absorption

4) It was measured by using 0.3971 N sodium hydroxide solution.

5) H. Nakajima, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **56**, 611 (1953).

spectra by a "Shimadzu" photometric spectrophotometer Type QB-50 using isopropyl alcohol as a solvent.

The authors are indebted to Mr. Michiaki Miura for technical assistance.

Department of Applied Chemistry
Faculty of Technology
Chiba University
Matsudo-shi, Chiba

Modified Bond Eigenfunction Method of Constructing Potential Energy Surface of Reaction. I. Theory and General Remarks

By Iwao YASUMORI

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In order to evaluate the chemical reaction rates theoretically, it is necessary to know the detailed feature of the interaction potential between the reacting species, i. e., the potential energy surfaces of the reaction. These surfaces are formed, in principle, from the eigenvalues of the wave equation for all electrons in the system at all orientations of atomic nuclei. Because of mathematical difficulties, however, which are the same as those in the calculation of "molecular energy", it is extremely difficult to construct the surface with the required accuracy, e. g., 0.1 kcal.

This situation of the problem has been a main cause of the fact that there is no available method for this purpose except Eyring's semi-empirical one[1] which is based on London's formula. Also it has been frequently pointed out by several investigators[2] that this approximate procedure contains many inadequacies, for instance, neglect of non-orthogonality between the orbitals of different atoms, introduction of *s*-electron approximation disregarding the direction of valence and the arbitrary choice of coulombic fraction ρ, etc. Nevertheless, this method has the distinctive character of giving an interpolation formula utilizing the experimental bond energies of component species.

Based on the idea of making use of the observed data for the component species, Moffitt[3] recently developed the "atoms-in-molecules" method in the field of "molecular theory" and succeeded in improving the calculated energy values for oxygen, ethylene, allyl radical, etc. If we regard the reacting system as a "complex molecule" and take molecular species as components, instead of atoms in Moffitt's method, it is possible to develop the corresponding "molecules-in-molecules" or "modified bond eigenfunction" method of constructing potential energy surfaces[4].

According to this idea, the author presents an improved method which stands on a firm basis and has wider applicability. The outline of the method and remarks on its application are given in this paper. The practical application and the inspection of the availability of the method will be made in relation to the hydrogen atom-molecule reaction in the following paper[5].

Theory

Elementary chemical reaction

$$A_1+B_1 \rightarrow A_2+B_2$$

is here considered, where A_1, B_1, A_2 and B_2 denote component molecular species. The potential energy surfaces of this reaction are constructed by the eigenvalues E of the wave equation for all n electrons,

$$\boldsymbol{H}\Psi(1,2,\cdots,n)=E(R_1,R_2,\cdots,R_N)\Psi(1,2\cdots,n) \quad (1)$$

1) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes", McGraw-Hill Book Co., Inc., New York (1941), p. 91.

2) H. M. James and A. S. Coolidge, *J. Chem. Phys.*, **1**, 825 (1933).

3) W. Moffitt, *Proc. Roy. Soc.*, **A210**, 224, 245 (1951); ibid., **A218**, 464, 486 (1953).

4) Also this idea has been independently found by Dr. P. Lykos, Argonne National Laboratory, U. S. A., private communication.

5) This series of papers contains the detailed account of the communication which was presented in *J. Chem. Phys.*, **23**, 1566 (1955).

at every set of fixed orientation of all N nuclei, $R_1, R_2, \cdots R_N$ in the system. Total Hamiltonian $\boldsymbol{H}$ has the usual form as

$$\boldsymbol{H}=-\sum_i\frac{1}{2}\Delta_i+\sum_{i>j}\frac{1}{r_{ij}}+\sum_{p>q}\frac{Z_pZ_q}{R_{pq}}-\sum_p\sum_i\frac{Z_p}{r_{pi}} \tag{2}$$

where p, q, and i, j, denote atomic nuclei and electrons, respectively; Z, nuclear charge, R and r, mutual distances between nuclei and electrons, respectively.

It is almost impossible to solve this equation in general; we must, therefore, be contented with merely some approximate solution. Now, when the distances between each species in the system become infinitely large, the wave function will have the following asymptotic form for any set of reactant or of any product, i.e., A_m+B_m, A_n+B_n,$\cdots$,

$$\Psi=\boldsymbol{A}\psi_{A_m^\mu}\cdot\psi_{B_m^\nu} \tag{3}$$

or

$$\Psi=\boldsymbol{A}\psi_{A_n^{\mu'}}\cdot\psi_{B_n^{\nu'}} \tag{3'}$$

$\psi_{A_m^\mu}$ and $\psi_{B_m^\nu}$ are the exact eigenfunctions of species A_m and B_m in the states μ and ν, respectively, and satisfy the equations

$$\boldsymbol{H}_{A_m}\psi_{A_m^\mu}=E_{A_m^\mu}\psi_{A_m^\mu} \tag{4}$$

and

$$\boldsymbol{H}_{B_m}\psi_{B_m^\nu}=E_{B_m^\nu}\psi_{B_m^\nu} \tag{4'}$$

where $\boldsymbol{H}_{A_m}$ and $\boldsymbol{H}_{B_m}$ are partial Hamiltonians for A_m and B_m, respectively, having the form of

$$\boldsymbol{H}_{A_m}=-\frac{1}{2}\sum_i\Delta_i+\sum_{i>j}\frac{1}{r_{ij}}+\sum_{p>q}\frac{Z_pZ_q}{R_{pq}}-\sum_p\sum_i\frac{Z_p}{r_{pi}} \tag{5}$$

and

$$\boldsymbol{H}_{B_m}=-\frac{1}{2}\sum_k\Delta_k+\sum_{k>l}\frac{1}{r_{kl}}+\sum_{r>s}\frac{Z_rZ_s}{R_{rs}}-\sum_s\sum_k\frac{Z_s}{r_{sk}} \tag{5'}$$

The nuclei p, q, and electrons i, j, belong to A_m and the nuclei r, s, and electrons k, l, to B_m. Also the eigenvalues $E_{A_m^\mu}$ and $E_{B_m^\nu}$ are those for the states of species, respectively. $\boldsymbol{A}$ in Eq. 3 is an antisymmetrizer[3] which makes the product functions $\psi_{A_m^\mu}\cdot\psi_{B_m^\nu}$ totally antisymmetrical for the exchange between any pair of electrons in the system, and has the form

$$\boldsymbol{A}=\{n!/n_A!\cdot n_B!\}^{1/2}\sum_t P_tv_t \tag{6}$$

where n_A, n_B and n are the numbers of electrons in A_m, B_m and their total respectively, P_t is any operator for inter-species exchange of electrons and $v_t=\pm1$ according to whether P_t gives an even or odd permutation.

Corresponding to all sets of species in their respective electronic states, $A_m^\mu+B_m^\nu$ $(m, \mu, \nu=1,2,\cdots)$, we take the "composite functions" defined by

$$\psi_{m\mu\nu}=\boldsymbol{A}\psi_{A_m^\mu}\cdot\psi_{B_m^\nu} \tag{7}$$

and we assume that the total wave function is constructed approximately from these sets of composite functions,

$$\Psi=\sum_{m,\mu,\nu}C_{m\mu\nu}\cdot\psi_{m\mu\nu} \tag{8}$$

The eigenvalues $E(R_1, R_2, \cdots, R_N)$ for each orientation of nuclei are given by

$$E=\int\bar{\Psi}\boldsymbol{H}\Psi\mathrm{d}\tau\Big/\int\bar{\Psi}\Psi\mathrm{d}\tau \tag{9}$$

When the usual variation method is adopted, the above relations are converted into the secular determinant,

$$\mathrm{Det.}\,|H_{m_\mu\nu,n_{\mu'}\nu'}-ES_{m\mu\nu,n\mu'\nu'}|=0 \tag{10}$$

where

$$H_{m\mu\nu,n\mu'\nu'}=\int\bar{\psi}_{m\mu\nu}\boldsymbol{H}\psi_{n\mu'\nu'}\mathrm{d}\tau \tag{11}$$

and

$$S_{m\mu\nu,n\mu'\nu'}=\int\bar{\psi}_{m\mu\nu}\psi_{n\mu'\nu'}\mathrm{d}\tau \tag{12}$$

Moreover, when we take an assumption of neglecting the contribution of spin angular momentum to the energy, the whole electronic state is classified with their total spin S and its component S_z values and the determinant is factorized into several smaller ones in which all the elements of H and S are those for the same electronic states $\kappa(S, S_z)$'s,

$$\mathrm{Det.}\,|H^\kappa_{m\mu\nu,n\mu'\nu'}-E^\kappa S^\kappa_{m\mu\nu,n\mu'\nu'}|=0 \qquad \kappa=1,2,\cdots \tag{13}$$

Next, let us divide the total Hamiltonian into the partial Hamiltonians $\boldsymbol{H}_{A_n}+\boldsymbol{H}_{B_n}$ for the composite species A_n+B_n and the remaining interaction term $\boldsymbol{I}_n$, that is,

$$\boldsymbol{H}=\boldsymbol{H}_{A_n}+\boldsymbol{H}_{B_n}+\boldsymbol{I}_n \tag{14}$$

where

$$\boldsymbol{I}_n=\sum_i\sum_k\frac{1}{r_{ik}}+\sum_p\sum_s\frac{Z_pZ_s}{R_{ps}}-\sum_p\sum_k\frac{Z_p}{r_{pk}}-\sum_s\sum_i\frac{Z_s}{r_{si}} \tag{15}$$

the nuclei p's and electrons i's belong to A_n and the nuclei s's and electrons k's to B_n. $\boldsymbol{H}_{A_n}$ and $\boldsymbol{H}_{B_n}$ have forms similar to $\boldsymbol{H}_{A_m}$ and $\boldsymbol{H}_{B_m}$, Eqs. 5 and 5'. Accordingly, $H^\kappa_{m\mu\nu,n\mu'\nu'}$ is rewritten as

$$H^{\kappa}_{m\mu\nu,\,n\mu'\nu'} = (EA^{\mu'}_{n} + EB^{\nu'}_{n})\,S^{\kappa}_{m\mu\nu,\,n\mu'\nu'} + I^{\kappa}_{m\mu\nu,\,n\mu'\nu'} \tag{16}$$

where

$$I^{\kappa}_{m\mu\nu,\,n\mu'\nu'} = \int \bar{\phi}_{m\mu\nu} \boldsymbol{I}_{n} \phi_{n\mu'\nu'} \mathrm{d}\tau \tag{17}$$

The number of bonds which take part in the reaction is usually one or two in each species and if we take an energy scale in which the bond energy of the composite state $A^{\mu'}_{n} + B^{\nu'}_{n}$, $\varepsilon_{n\mu'\nu'}$ is measured from the state where all these "reacting bonds" break down and the species A_n and B_n are separated into several fragments (radicals), then the eigenvalues for the composite state is described as a sum of "fragment-state energy" $E_{n\mu'\nu'}$ and "bond energy" $\varepsilon_{n\mu'\nu'}$

$$E_{A^{\mu'}_{n}} + E_{B^{\nu'}_{n}} = E_{n\mu'\nu'} + \varepsilon_{n\mu'\nu'} \tag{18}$$

Further, we take conveniently one of these "fragment-states" as a standard state and define its energy, E^{κ}_{0}. For this standard, the energies of the whole system E and of any composite state which belongs to the same $\kappa(S, S_z)$, $E_{A^{\mu'}_{n}} + E_{B^{\nu'}_{n}}$, are rewritten as follows:

$$E^{\kappa} = E^{\kappa}_{0} + \varepsilon^{\kappa} \tag{19}$$

and

$$E_{A^{\mu'}_{n}} + E_{B^{\nu'}_{n}} = E^{\kappa}_{0} + \varepsilon^{\kappa}_{n\mu'\nu'} = E^{\kappa}_{0} + (\varepsilon_{A^{\mu'}_{n}} + \varepsilon_{B^{\nu'}_{n}}) \tag{20}$$

ε^{κ}, $\varepsilon^{\kappa}_{n\mu'\nu'}$, $\varepsilon_{A^{\mu'}_{n}}$ and $\varepsilon_{B^{\nu'}_{n}}$ in Eqs. 19 and 20 are respective "bond energies" of the system, of the composite state and of the species A_n and B_n newly measured from the level E_0. Substituting Eqs. 16, 19 and 20 into 10,

$$\mathrm{Det.}\,|I^{\kappa}_{m\mu\nu,\,n\mu'\nu'} + (\varepsilon^{\kappa}_{n\mu'\nu'} - \varepsilon^{\kappa})\,S_{m\mu\nu,\,n\mu'\nu'}| = 0 \tag{21}$$

is obtained finally. Since $\varepsilon_{A^{\mu'}_{n}}$ and $\varepsilon_{B^{\nu'}_{n}}$ in Eq. 20 are bond energies[6] for molecules, we can frequently utilize their observed values[7]. The remaining unknown quantities, $S_{m\mu\nu,\,n\mu'\nu'}$ and $I_{m\mu\nu,\,n\mu'\nu'}$ can be evaluated, in principle, if we know the exact forms of the composite functions. Unfortunately, this is not the case except for a few states of hydrogen molecule and also the direct use of the function in exact form for the present purpose is unsuitable because of complicated calculations. Therefore, we may use their values calculated by the use of approximate composite functions with a simple analytic form[8].

Some Limitations for the Composite Functions

According to the above considerations the reactions proceed "adiabatically" on each surface. It is expected that this adiabatic condition brings some limitations on the character of states (wave functions) of species to be combined. Furthermore, when the reacting system has some symmetrical configurations during the reaction, the limitations become finer. This correlation between limited states of species was recently studied by Shuler and Laidler for the polyatomic system by the use of spin and orbital correlation rules[9,10].

Their conclusion shows that three or four atomic systems lie frequently on a

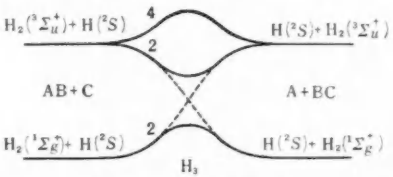

Fig. 1a. Lower potential energy surfaces of H-H-H system.

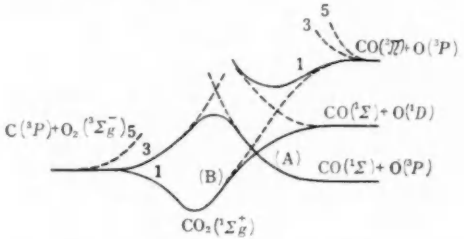

Fig. 1b. Lower potential energy surfaces of C-O-O system.

6) Here, the definition of "bond energy" is used also for the energy of the repulsive state of a molecule.

7) For example, when A_n is a diatomic molecule, some of its bond energies are given as functions of nuclear distance based on the spectroscopic data. (Morse function etc.)

8) The matrix, $\boldsymbol{H} = \boldsymbol{I} + E\boldsymbol{S}$, is not always Hermitian in this case. In order to avoid this theoretial defect, adoption of approximation for the elements such as

$$\bar{H}_{m\mu\nu,\,n\mu'\nu'} = \bar{H}_{n\mu'\nu',\,m\mu\nu}$$

$$\frac{1}{2}[H_{m\mu\nu,\,n\mu'\nu'} + H_{n\mu'\nu',\,m\mu\nu}]$$

may be required. Similar cosideration also has been given by Moffitt. See Ref. 3.

9) K. E. Shuler, *J. Chem. Phys.*, **21**, 624 (1953).

10) K. J. Laidler, ibid., **22**, 1740 (1954).

straight line or a plane where the orbital correlation may have an important part, while the general polyatomic system scarcely has these constraints at all as long as special symmetry does not exist. These results and the correlation tables given by Shuler[9] are available for the present consideration. Typical examples of correlation for the lower energy surfaces are shown in Fig. 1. In the figure, the numbers on the curves representing adiabatic surfaces are for spin multiplicity, $2S+1$, and the states of reactants and resultants are shown in both ends of each curve. Relative orientation and shapes of the curves are arbitrary.

Some explanations are added to the system H_3 (Fig. 1a). The lowest surface of this reaction is clearly one of doublet. When all the nuclei are orientated on a line, the system has a symmetry of $C_{\infty v}$ and so the lowest state will be classified to $^2\Sigma^+$. Then the states of composite species which satisfy this designation are confined

$$H_2(^{1,3}\Sigma^+)+H(^2S_g),\quad H_2(^{1,3}\Sigma^+)+H(^2P_u)$$
$$H_2(^{1,3}\Pi)+H(^2P_u),\ \text{etc.}$$

However, it is known that elements, $S_{m\mu\nu,\,n\mu'\nu'}$ and $I_{m\mu\nu,\,n\mu'\nu'}$ which relate to states of higher energy hardly contribute to the lowest state, so we can conveniently neglect these composite states of high energy and can reduce the order of the determinant. Further, when this system has higher symmetries such as equidistance-on-a-line ($D_{\infty h}$) or equilateral triangle (D_{3h}), new relations appear among the coefficients of composite functions $C_{m\mu\nu}$'s, so as to reduce the order of determinant[11].

As for the C–O–O system, the reaction, $CO_2(^1\Sigma^+)\rightarrow CO(^1\Sigma)+O(^3P)$ is a forbidden process in the present treatment. The intersection of the surfaces A and B in Fig. 1b will give, however, the zeroth approximation for the surface of this reaction.

Approximate Estimation of $S_{m\mu\nu,\,n\mu'\nu'}$ and $I_{m\mu\nu,\,n\mu'\nu'}$ for the Three-atom System

Discussion is focused here on the reaction, as an example,

$$AB+C\rightarrow A+BC\quad\text{or}\quad AC+B$$

which is composed of three atoms having one valence electron. One of composite functions which express its lowest state with $S=1/2$ and $S_z=1/2$ is

$$\psi_1=\boldsymbol{A}\psi_{AB}(1,2)\cdot\psi_C(3)$$
$$=\sum_n P_c^n\varphi_{AB}(1,2)\cdot\varphi_C(3)$$
$$\times\frac{1}{\sqrt{2}}\{\alpha(1)\beta(2)-\alpha(2)\beta(1)\}\cdot\alpha(3)\quad(22)$$

where P_c means cyclic exchange of electrons 1, 2 and 3 in this order; φ's are the orbital parts and the bond orbital, $\varphi_{AB}(1,2)$, is symmetrical for the exchange of electrons 1 and 2. Analogous forms are taken for the functions ψ_2 and ψ_3 of other composite states, BC+A and CA+B, respectively.

Now, we neglect the contributions from all higher composite states and assume φ_{AB}, φ_{BC},$\cdots$, and φ_A, φ_B,$\cdots$, to be the ones of their lowest states, and then the order of determinant can be reduced to three. We take, furthermore, the simplest form of these functions by the use of atomic orbital approximation,

$$\varphi_{AB}(1,2)=a(1)b(2)+a(2)b(1)\quad(23)$$

and

$$\varphi_C(3)=c(3)\quad(24)$$

and so on. In these functions, $a(1)$, $b(2)$ and $c(3)$ express the valence orbitals of atom A, B and C, respectively. By the use of these expressions, the formulae of S_{mn} and I_{mn} (m, $n=1$, 2, 3) are described as shown in the Appendix.

Since the numerical values of molecular integrals including atomic orbitals with the principal quantum number $n=1,2,3$ are available at present[12], it is possible to evaluate the formulae directly except for several multiple-center integrals. Also these integrals are estimated exactly for some simple systems and also are approximately given by, e.g., Rudenberg-Mulliken's procedure[13].

Here, it is interesting to examine the simplification neglecting all these multiple-center integrals in the formulae. In this case, I_{mn} can be described as the function of coulombic energies Q_{AB}, Q_{BC},$\cdots$, and exchange energies J_{AB}, J_{BC},$\cdots$, of respective bonds, AB, BC,$\cdots$, for example,

$$I_{11}=2Q_{CA}+Q_{BC}-J_{CA}-J_{BC}$$

where

$$Q_{CA}=\overline{R}_{CA}^{-1}+(c^2|a^2)-(c^2|A)-(a^2|C)^{14}$$

11) See, for example, H. Eyring, J. Walter and G. E. Kimball, "Quantum Chemistry", John Wiley & Sons, Inc., New York (1949), Chap. X, p. 172; Chap. XIII, p. 252.

12) M. Kotani, A. Amemiya, E. Ishiguro and T. Kimura, "Table of Molecular Integrals", Maruzen Co., Ltd., Tokyo (1955).

13) K. Rudenberg, *J. Chem. Phys.*, **19**, 1433 (1951); R. S. Mulliken and R. G. Parr, ibid., **18**, 1338 (1950).

and

$$J_{CA}=(ac)^2\bar{R}_{CA}^{-1}+(ac|ac)-(ac)(ac|A+C),$$

etc.

Moreover, when the non-orthogonality between orbitals of different atoms is disregarded in S_{mn}'s, the expressions for I_{mn}'s and S_{mn}'s exactly correspond to those obtained by the well-known method of bond eigenfunction[15].

Eyring's semi-empirical method is derived readily by the use of these expressions and by taking the values of Q_{AB}, $J_{AB},\cdots$, from the assumption,

$$\varepsilon_{AB}=Q_{AB}+J_{AB},\quad \varepsilon_{BC}=Q_{BC}+J_{BC},\cdots, \tag{25}$$

and

$$\rho_{AB}=Q_{AB}/\varepsilon_{AB},\quad \rho_{BC}=Q_{BC}/\varepsilon_{BC},\cdots, \tag{26}$$

where ε_{AB}, $\varepsilon_{BC},\cdots$ and ρ_{AB}, $\rho_{BC},\cdots$ are bond energies and coulombic fractions of bonds AB, $BC,\cdots$. Therefore, this procedure may be regarded as one of the methods for estimating the elements I_{mn}'s conveniently by the use of ε_{AB}'s and ρ_{AB}'s.

Another basis of the present method will be examined below with respect to this reaction example. It is known theoretically that the wave functions which express the doublet states with $S_z=1/2$ are written as follows, by the use of orbital approximation;

$$\Phi_1=\sum_n P_c^n\{\psi(1,2,3)+\psi(2,1,3)\}\times\frac{1}{\sqrt{2}}\{\alpha(1)\beta(2)-\alpha(2)\beta(1)\}\alpha(3) \tag{27}$$

and

$$\Phi_2=\sum_n P_c^n\{(\psi1,2,3)-\psi(2,1,3)\}\times\frac{1}{\sqrt{6}}[\{\alpha(1)\beta(2)+\alpha(2)\beta(1)\}\alpha(3)-2\alpha(1)\alpha(2)\beta(3)] \tag{28}$$

where $\psi(1,2,3)$ is the orbital function[16]. When we take the simplest form of ψ's, $\psi(1,2,3)=a(1)b(2)c(3)$, etc., Φ_1 is identified with the composite function $A\psi_{AB}\cdot\psi_C$ and Φ_2 is also rewritten as

$$\Phi_2=\sum_n P_c^n\{a(1)b(2)-a(2)b(1)\}c(3)\times\frac{1}{\sqrt{6}}[\{\alpha(1)\beta(2)+\alpha(2)\beta(1)\}\alpha(3)-2\alpha(1)\alpha(2)\beta(3)] \tag{29}$$

or

$$=\sum_n P_c^n[\{b(1)c(2)+b(2)c(1)\}a(3)+\{c(1)a(2)+c(2)a(1)\}b(3)]\times\frac{1}{\sqrt{6}}\{\alpha(1)\beta(2)-\alpha(2)\beta(1)\}\alpha(3) \tag{29'}$$

These expressions correspond apparently to the state composed of AB in a triplet state and C in a doublet state or the combination of composite states, BC in a singlet state and A in a doublet state, and CA and B in the analogous states.

Since the eigenvalues of these doublet states of the whole system are determined from the wave function,

$$\Psi=c_1\Phi_1+c_2\Phi_2 \tag{30}$$

the utilization of Φ_1 and Φ_2 as the basic functions is equivalent to the adoption of the set of composite functions, $A\psi_{AB}\cdot\psi_C$, $A\psi_{BC}\cdot\psi_A$ and $A\psi_{CA}\cdot\psi_B$.

The conclusion from the above consideration and also the method of bond-eigenfunction shows that one of these three functions is linearly dependent on the others. But, in the present method, such a relation does not always hold, for the present choice of a functional set is effectively to make use of the observed values of bond energies, ε_{AB}, ε_{BC} and ε_{CA}.

Remarks on the Application to the General System

In several reactions, bonds have frequently a directional character such as p-, d- orbitals or their hybridization. Also other important cases are the reactions in multielectronic systems with inner-shell and incompleted shell electrons. Any polyatomic system is comprised in the combination of these cases. Some remarks will be made on the application to these systems.

System with Directed Valence Bond. — A typical example is the hydrogen-halogen reaction

$$X(^2P)+H_2(^1\Sigma^+)\rightarrow HX(^1\Sigma^+)+H(^2S)$$

For simplicity, the halogen atom is assumed to have only a p-valence electron. This system has been studied only by Magee with crude approximation[17].

Denoting two independent p-orbitals of halogen, which lie on the plane involving three atoms, by p_x and p_y, we can readily see that these p-orbitals and s-orbitals of two hydrogen atoms form a basis for an

14) For these notations, see the definitions given in Appendix.
15) Ref. 11, Chap. XIII, p. 232.
16) Ref. 12, p. 15.
17) J. L. Magee, *J. Chem. Phys.*, **8**, 677 (1940).

irreducible representation of the group of surface symmetry C_s. Accordingly, the p-bonding orbital on the plane is expressed by linear combination of p_x and p_y,

$$p_\sigma = \lambda p_x + \mu p_y \tag{31}$$

Since the total wave function is described as

$$\Psi = C_1 \boldsymbol{A}\psi_{XH_A}\cdot\psi_{H_B} + C_2\boldsymbol{A}\psi_{XH_B}\cdot\psi_{H_A} + C_3\boldsymbol{A}\psi_{H_2}\cdot\psi_X \tag{32}$$

respective bond functions are given by

$$\psi_{XH_A} = \lambda_1\psi(p_x - h_A) + \mu_1\psi(p_y - h_A)$$

$$\psi_{XH_B} = \lambda_2\psi(p_x - h_B) + \mu_2\psi(p_y - h_B)$$

and $\psi_X = \lambda_3\psi(p_x) + \mu_3\psi(p_y)$

where h's are the valence orbitals of the hydrogen atom.

Even if all states of higher energy are neglected, the determinant is still so great. But when the ratios λ_i/μ_i's are fixed so as to minimize the energy of each composite state, the order of determinant can be reduced to three and the bond energy of HX is utilized effectively, for the p_σ orbital lies along the line joining H and X in this case[18].

System with Inner-shell Electrons. — The simplest example is the reaction including alkali metal,

$$LiH(^1\Sigma^+) + H(^2S) \rightarrow Li(^2S) + H_2(^1\Sigma^+)$$

of which one of the composite functions is

$$\phi_1 = \boldsymbol{A}\psi_{LiH}(1,2,3,4)\cdot\psi_H(5)$$

The orbital part of molecular function, ψ_{LiH} may be factorized by the use of the inner shell orbital ϕ_i[19] and the bond orbital ϕ_{LiH} which are symmetrical for exchange of electrons, respectively. Expressing these orbitals by the introduction of atomic orbital approximation, it is found that I_{mn}'s consist of two parts, (1) integrals with exchange of electrons between inner-shell and bond orbitals of other species and (2) integrals in which inner-shell electrons remain un-exchanged.

Now, we take a simplification neglecting the former because of the small overlapping between inner-shell and valence orbital of different species. The electrons in closed shell distribute almost spherically round the Li nucleus and then contribute to energy only by coulombic repulsion. Since this effect is estimated effectively by adjusting the nuclear charge of Li atom, the system is regarded as the one consisting of three valence electrons only.

The effect of an incomplete shell, lone pair and even that of radicals which are not concerned directly with the reaction, are similar in principle to the above case. However, an important difference between them is that the charge distributions in these cases are not spherically symmetrical for the nuclei noticed. Therefore, it may be necessary to take such an approximation as the replacement of these distributions to several point charges distributed around the nucleus.

Finally, a remark is briefly made on the system having multiple bond. When the bond breaks completely or is newly formed as a result of reaction, all electrons relating to the bond must be taken into the treatment. On the other hand, when the bond is partially subjected to reaction, electrons in the remaining part of the bond behave in the same manner as those of the incompleted shell stated above and then are treated in a similar way too. The above consideration has been taken for the displacement reaction $A+BC \rightarrow AB+C$. Conclusions obtained here, however, are readily extended to other types of reaction, for instance, double decomposition, $AB+CD \rightarrow AC+BD$.

If the ground states of molecules are all singlet in this case, the lowest surface will also belong to singlet and composite functions, which can be constructed in a way quite analogous to that shown in the previous sections.

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Laboratory of Physical Chemistry
Tokyo Institute of Technology
Meguro-ku, Tokyo

Appendix

Formulae of S_{mn} and I_{mn} for the System of Three Atoms with One Valence Electron. — In a way similar to ϕ_1 of Eq. 22, ϕ_2 and ϕ_3 for the other composite states are described as follows:

18) When the direction of the valence orbital is fixed during the reaction for some reason, for example, the hindrance of atoms or radicals attached to the noticed atom, and it does not accord with the joining line, some correction may be required for full insertion of observed bond energies.

19) This orbital almost coincides with inner shell orbital of Li atom.

$$\psi_2 = \boldsymbol{A}\psi_{BC}(1,2)\cdot\psi_A(3)$$

and $$\psi_3 = \boldsymbol{A}\psi_{CA}(1,2)\cdot\psi_B(3)$$

Total Hamiltonian operator and wave function are

$$\boldsymbol{H} = -\frac{1}{2}\sum_{i=1}^{3}\Delta_i + \sum_{i>j}\frac{1}{r_{ij}} + \sum_{p>q}\frac{Z_pZ_q}{R_{pq}} - \sum_p\sum_i\frac{Z_p}{r_{pi}} \tag{A.1}$$

and

$$\Psi = C_1\psi_1 + C_2\psi_2 + C_3\psi_3 \tag{A.2}$$

Accordingly, the determinant to be solved is

$$\text{Det.}\,|I_{mn} + (\varepsilon_{mn} - \varepsilon)S_{mn}| = 0 \quad m,n = 1,2,3 \tag{A.3}$$

I_{mn}'s are further resolved into several terms for convenience,

$$I_{mn} = K_{mn} - J_{mn} + R_{mn}\cdot S_{mn} \tag{A.4}$$

The formulae of ε_{mn}, S_{mn}, R_{mn}, K_{mn} and J_{mn} are shown below. The notation of integrals used in the expressions is as follows:

$$(ab) = \int a(1)b(1)\,d\tau_1$$

$$(a^2|b^2) = \int a^2(1)\frac{1}{r_{12}}b^2(2)\,d\tau_1 d\tau_2$$

$$(ab|ab) = \int a(1)b(1)\frac{1}{r_{12}}a(2)b(2)\,d\tau_1 d\tau_2$$

$$(a^2|P) = \int a^2(1)\cdot\frac{Z_B}{r_{B1}}\,d\tau_1 \qquad \text{etc.}$$

Also, in the expressions below, ε_{m1} $(A \rightleftarrows C)$ means the exchange of letters "A" and "C" in that of ε_{m1} and so on.

(1) ε_{mn}; $\varepsilon_{m1} = \varepsilon_{AB}$

$\varepsilon_{m2} = \varepsilon_{m1}(A \rightleftarrows C)$ $\quad m = 1,2,3$

$\varepsilon_{m3} = \varepsilon_{m1}(B \rightleftarrows C)$

(2) R_{mn}; $R_{m1} = \bar{R}_{BC}^{-1} + \bar{R}_{AC}^{-1}$ $\quad \bar{R}_{BC}^{-1} = Z_BZ_C\cdot R_{BC}^{-1}$ etc.,

$R_{m2} = R_{m1}(A \rightleftarrows C)$ $\quad m = 1,2,3$

$R_{m3} = R_{m1}(B \rightleftarrows C)$

(3) S_{mn}; $S_{11} = 2 + 2(ab)^2 - (bc)^2 - (ac)^2 - 2(ab)(bc)(ca)$

$S_{22} = S_{11}(a \rightleftarrows c)$

$S_{33} = S_{11}(b \rightleftarrows c)$

$S_{12} = S_{21} = -1 + 2(ac)^2 - (ab)^2 - (bc)^2 + (ab)(bc)(ca)$

$S_{13} = S_{31} = S_{12}(a \rightleftarrows b)$

$S_{23} = S_{32} = S_{12}(b \rightleftarrows c)$

(4) K_{mn}; $K_{11} = 2(a^2|c^2) + 2(b^2|c^2) + 4(ab)(ab|c^2) - (ac|ac) - (bc|bc) - (bc)\cdot\{(a^2|bc) + (ab|ac)\} - (ac)\{(b^2|ac) + (ab|bc)\} - 2(ab)(ac|bc)$

$K_{22} = K_{11}(a \rightleftarrows c)$

$K_{33} = K_{11}(b \rightleftarrows c)$

$K_{12} = 2[(ac|ac) + (ac)(b^2|ac)] + (bc)(ab|ac) + (ab)(bc|ac) - [(a^2|c^2) + (b^2|a^2) + (ab|ab) + (ab)(c^2|ab) + (ac)(bc|ab) + (bc)\{2(bc|a^2) + (ab|ac)\}]$

$K_{32} = K_{12}(b \rightleftarrows c)$

$K_{21} = K_{12}(a \rightleftarrows c)$

$K_{31} = K_{21}(a \rightleftarrows b)$

$K_{13} = K_{12}(a \rightleftarrows b)$

$K_{23} = K_{13}(a \rightleftarrows c)$

(5) J_{mn}; $J_{11} = \{2-(bc)^2\}\cdot(a^2|C) + \{2-(ac)^2\}\cdot(b^2|C) + \{4(ab) - 2(ac)(bc)\}\cdot(ab|C) + \{2+2(ab)^2\}\cdot(c^2|A+B) - \{(bc) + (ab)(ac)\}\cdot(bc|A+B+C) - \{(ac) + (ab)(bc)\}\cdot(ac|A+B+C)$

$J_{22} = J_{11}(a \rightleftarrows c,\ A \rightleftarrows C)$

$J_{33} = J_{11}(b \rightleftarrows c,\ B \rightleftarrows C)$

$J_{12} = \{2(ac) + 2(ab)(bc)\}(ac|B+C) - \{(ab) + (ac)(bc)\}(ab|B+C) - \{1+(bc)^2\}(a^2|B+C) - \{1+(ab)^2\}(c^2|A) - \{1-2(ac)^2\}(b^2|A) + \{2(ac) - (ab)(bc)\}(ac|A) + \{(ac)(ab) - 2(bc)\}(bc|A) + \{2(bc)(ac) - (ab)\}(ab|A)$

$J_{32} = J_{12}(b \rightleftarrows c,\ B \rightleftarrows C)$

$J_{21} = J_{12}(a \rightleftarrows c,\ A \rightleftarrows C)$

$J_{31} = J_{21}(a \rightleftarrows b,\ A \rightleftarrows B)$

$J_{13} = J_{12}(a \rightleftarrows b,\ A \rightleftarrows B)$

$J_{23} = J_{13}(a \rightleftarrows c,\ A \rightleftarrows C)$

Modified Bond Eigenfunction Method of Constructing Potential Energy Surface of Reaction. II. Application to the Hydrogen Atom-Molecule Reaction

By Iwao YASUMORI

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A new method of constructing the potential energy surface of a chemical reaction was presented in the previous paper and some remarks on the procedure of application were also given. In order to examine its availability, the method is effectively applied to the hydrogen atom-molecule reaction, since much theoretical and experimental knowledge has been accumulated on its component species, H_2 and H.

As is well known, the potential energy surfaces of this reaction have been evaluated by Hirschfelder et al.[1] in a purely theoretical manner and by Eyring et al.[2] semi-empirically. Also, recently several investigators[3] have given some considerations about this system from the standpoint of molecular orbital method.

In this paper, besides the examination of the applicability of the method, surface properties obtained here are discussed comparing them with those obtained in the previous works. Calculation of reaction rate based on the surface is carried out also.

Composite Wave Functions

We denote three hydrogen atoms in the systems, A, B and C, and, for simplicity, confine ourselves to the lowest surface of linear configuration. Therefore, it is assumed that the reaction proceeds by the equation

$$H_AH_B+H_C \rightarrow H_A+H_BH_C$$

on a straight line.

According to the considerations given in Paper 1, the total wave function which expresses the state with the total spin $S=1/2$ and its component $S_z=1/2$ is described as follows:

$$\begin{aligned}\Psi=\sum_{m=1}^{3} C_m\psi_m &= C_1\boldsymbol{A}\varphi_{AB}(1,2)\varphi_C(3)\\ &\times\frac{1}{\sqrt{2}}\{\alpha(1)\beta(2)-\alpha(2)\beta(1)\}\alpha(3)\\ &+C_2\boldsymbol{A}\varphi_{BC}(1,2)\varphi_A(3)\\ &\times\frac{1}{\sqrt{2}}\{\alpha(1)\beta(2)-\alpha(2)\beta(1)\}\alpha(3)\\ &+C_3\boldsymbol{A}\varphi_{CA}(1,2)\varphi_B(3)\\ &\times\frac{1}{\sqrt{2}}\{\alpha(1)\beta(2)-\alpha(2)\beta(1)\}\alpha(3)\end{aligned} \tag{1}$$

where each term represents the composite functions for bond structures $AB+C$, $BC+A$ and $CA+B$, respectively. In the equation, $\varphi_{AB}(1,2),\cdots$ are ${}^1\Sigma^+_g$ orbital functions of H_2 and $\varphi_C(3),\cdots$ are atomic $1s$ orbital functions of hydrogen. Spin functions $\frac{1}{\sqrt{2}}\{\alpha(1)\beta(2)-\alpha(2)\beta(1)\}$ and $\alpha(3)$ correspond to singlet state of molecule and doublet state of atom, respectively. There are many higher energy states which correlate to the lowest surface such as $H_2({}^{1,3}\Sigma^+)+H({}^2S_g,{}^2P_u)$, $H_2({}^{1,3}\Pi)+H({}^2P_u)$, etc. But all these composite states were excluded in the present calculation[4], since, apart from the simplification of procedure, their contributions to the energy of the lowest state are rather small and also some of them are hardly available because of the lack of experimental data.

By the operation of antisymmetrizer,

$$\boldsymbol{A}=\frac{1}{\sqrt{3}}\Sigma_i P_i v_i \tag{2}$$

each composite function is expressed as

$$\begin{aligned}\psi_1=&\frac{1}{\sqrt{6}}\varphi_{AB}(1,2)\cdot\varphi_C(3)\{\alpha(1)\beta(2)-\alpha(2)\beta(1)\}\alpha(3)\\ &+\frac{1}{\sqrt{6}}\varphi_{AB}(2,3)\cdot\varphi_C(1)\{\alpha(2)\beta(3)-\alpha(3)\beta(2)\}\alpha(1)\\ &+\frac{1}{\sqrt{6}}\varphi_{AB}(3,1)\cdot\varphi_C(2)\{\alpha(3)\beta(1)-\alpha(1)\beta(3)\}\alpha(2)\end{aligned} \tag{3}$$

and so on. The determinant, from which energy values for all configurations of atoms are deduced, is described as

$$\text{Det.}\,|I_{mn}+(\varepsilon_{mn}-\varepsilon)S_{mn}|=0 \qquad m,n=1,2,3 \tag{4}$$

1) J. O. Hirschfelder, N. Rosen and H. Eyring, *J. Chem. Phys.*, **4**, 121 (1936).
2) J. O. Hirschfelder, H. Eyring and B. Topley, ibid., **4**, 170 (1936).
3) J. M. Walsh and F. A. Matsen, ibid., **19**, 526 (1951); V. Griffing and J. T. Vanderslice, ibid., **23**, 1035 (1955); G. E. Kimball and J. G. Trulio, ibid., **28**, 493 (1958).
4) However, the composite states $H_2({}^3\Sigma^+_u)+H({}^2S_g,1s)$, are automatically included in the wave function. See Paper I.

where $$S_{mn}=\int \bar{\psi}_m \psi_n d\tau \quad (5)$$

$$I_{mn}=\int \bar{\psi}_m \boldsymbol{I}_n \psi_n d\tau \quad (6)$$

When we take the lowest state of free atoms 3H as a standard of energy of system, bond energies of species are given by

$$\varepsilon_{m1}=\varepsilon_{H_2}(AB),\quad \varepsilon_{m2}=\varepsilon_{H_2}(BC),\quad \varepsilon_{m3}=\varepsilon_{H_2}(CA)$$
$$m=1,2,3$$

and interaction operators $\boldsymbol{I}_n$'s are also defined as

$$\boldsymbol{I}_1=\boldsymbol{H}-\boldsymbol{H}_{AB}-\boldsymbol{H}_C \quad (7)$$
$$\boldsymbol{I}_2=\boldsymbol{H}-\boldsymbol{H}_{BC}-\boldsymbol{H}_A \text{ and } \boldsymbol{I}_3=\boldsymbol{H}-\boldsymbol{H}_{CA}-\boldsymbol{H}_B$$

where $\boldsymbol{H}$ is the total Hamiltonian of three electrons in the system and $\boldsymbol{H}_{AB}$ and $\boldsymbol{H}_C$ are the partial ones for molecule AB and atom C, respectively, and so on.

Molecular functions taken into the calculation are as follows:

(a) Heitler-London type function,

$$\varphi_{AB}(1,2)=a(1)b(2)+a(2)b(1)$$

where $a(1)$ and $b(2)$ are 1s orbital functions of hydrogen,

$$a(1)=(1/\pi)^{1/2}\exp(-r_{A1})$$

and $$b(2)=(1/\pi)^{1/2}\exp(-r_{B2}),\text{ etc.}$$

(b) Wang type function obtained by introduction of effective nuclear charge z into the atomic orbitals of the function a,

$$a(1)=(z^3/\pi)^{1/2}\exp(-zr_{A1})\quad \text{etc.}$$

(c) Weinbaum type function composed of the above functions, that is, the covalent term, and the ionic term,

$$\varphi^{ion}_{AB}(1,2)=a(1)a(2)+b(1)b(2)$$

Since these functions are described by the use of atomic orbital approximation, formulae of elements I_{mn} and S_{mn} given in the Appendix of Paper I are available for the present calculation. In addition to this, it is to be noted that when we estimate the values of ε_{H_2} also by the use of these approximate functions, the results are reduced to those of Hirschfelder et al.[1] The present method differs from theirs in the point that the interaction energies are evaluated by making use of approximate functions, while the observed values, that is, those deduced from the exact functions, are utilized for the bond energies of H_2.

Details of Calculation and Results

Detailed procedure of energy calculations which were performed by the use of approximate functions are shown below for the respective cases.

(a) Calculation of Symmetrical Linear Configuration with Heitler-London Type Function of H_3.—Making use of the formulae in the Appendix of Paper I, we can express the elements S_{mn} and I_{mn} as the sum of several molecular integrals, i. e., two-center and three-center ones. The values of two-center integrals were obtained from the tables by Kotani et al.[5] and by Hirschfelder and Linnett[6] (being abbreviated to L.-H. hereafter). For the three-center integrals, values of one electron integrals such as

$$(bc\mid A)=\int b(1)c(1)\frac{1}{r_{A1}}d\tau_1$$

were taken from the table by Hirschfelder and Weygandt[7] and values of two electron ones, for example,

$$(bc\mid a^2)=\int b(1)c(1)\frac{1}{r_{12}}a^2(2)d\tau_1 d\tau_2$$

were calculated in a similar way as those of Hirchfelder's[1].

Also some of their values were taken from the table in the paper of Baker et al.[8] Therefore, such an approximate calculation as Rudenberg-Mulliken's procedure[9],

$$(bc\mid a^2)\simeq\frac{1}{2}(bc)\cdot[(b^2\mid a^2)+(c^2\mid a^2)]\quad \text{etc.},$$

was not required in this case.

(b) Calculation with Heitler-London-plus-Ionic Type Function.—Strictly speaking, the coefficient of ionic term added to covalent function must be taken so as to minimize the energy value, since the ionic term is another function contributing $^1\Sigma^+$ state of molecule. However, the coefficient was fixed to the value, $C_{ion}=0.1607$ take from L.-H.'s work, in order only to examine the effect of electronic distribution in hydrogen molecular function. In this case, the ionic integrals of two-center type, for example,

$$(ac\mid a^2)=\int a(1)c(1)\frac{1}{r_{12}}a^2(2)d\tau_1 d\tau_2\quad \text{etc.},$$

newly appear. The values were obtained also from the table by Kotani et al.

(c) Calculation with Wang Type Function.—At the values of effective nuclear charge in atomic orbital function, the following values were used for the calculation; (i) the values from original Wang function, $z=1.166$[10] and (ii) the values from L.-H.'s work shown in Table I.

When we adopt these functions for the strict procedure of calculation, the molecular integrals which appear, are of unsymmetrical type including the atomic orbital functions with effective nuclear charge, z and $z=1$. The values of these

5) M. Kotani, A. Amemiya, E. Ishiguro and T. Kimura, "The Table of Molecular Integrals", Maruzen Co., Ltd., Tokyo (1955); M. Kotani, A. Amemiya and T. Simose, *Proc. Phys.-Math. Soc. Japan*, **20**, Extra 1 (1938); **22**, Extra 1 (1940).

6) J. O. Hirschfelder and J. W. Linnett, *J. Chem. Phys.*, **18**, 130 (1950).

7) J. O. Hirschfelder and C. N. Weygandt, ibid., **6**, 806 (1938).

8) R. S. Baker, H. Eyring, C. J. Thorne and D. A. Baker, ibid., **22**, 699 (1954).

9) K. Rudenberg, ibid., **19**, 1433 (1951); R. G. Parr and R. S. Mulliken, ibid., **18**, 1338 (1950).

10) S. C. Wang, *Phys. Rev.*, **31**, 579 (1928).

TABLE I. VARIATION OF z WITH INTERNUCLEAR SEPARATION IN THE WANG TYPE FUNCTION OF H_2

zR(a. u.)*	1.0	1.5	1.75	2.0	2.5	3.0
z	1.3911	1.2145	1.1388	1.0823	1.0151	1.0000

* 1 a. u.=0.5292 Å.

unsymmetrical integrals were estimated accurately by James[11] for 1s and 2s orbitals of lithium atom and approximately be Mulligan[12] for carbon dioxide calculation. Here, for simplicity, the effective nuclear charges in all orbitals were assumed to be equally z, so as to utilize the results of calculations a) and b). The effect of this approximation will be discussed later.

(d) Calculation with Wang-plus-Ionic Type Function.—Used values of effective nuclear charge and coefficients of ionic term are as follows: (i) the values used in original Weinbaum's function[13], $z=1.193$ and $C_{ion}=0.256$ and (ii) the values obtained from L.-H's treatment of H_2 which are shown in Table II.

TABLE II. VARIATION OF z AND C_{ion} IN THE WANG-PLUS-IONIC TYPE FUNCTION OF H_2

zR(a. u.)	1.0	1.5	1.75	2.0	2.5	3.0
z	1.3976	1.2411	1.1746	1.1195	1.0472	1.0000
C_{ion}	−0.01603	0.1361	0.1664	0.1780	0.1681	0.1200

Further calculations were performed for the following cases.

(e) Effect of Varying Nuclear Charge z.—For the linear configuration of equi-distance, calculation was carried out varying z in Wang type function as $z=1.0$, 1.166, 1.3, 1.4 and 1.5, respectively.

(f) Comparison of Energy Values on Various Stages of Approximation.—The effects of various approximations such as (i) use of three-center integral values calculated by Rudenberg-Mulliken type approximation, (ii) neglect of these integrals and (iii) ii plus neglect of non-orthogonality of orbitals in S_{mn}'s, were examined utilizing Heitler-London type function for the same configuration as described in e).

(g) Variaton of Energy by Bending.—Increase of energy owing to bend of R_{BC} to R_{AB} was calculated for several equi-distant configurations by the use of Heitler-London and Wang type functions.

(h) Energy Values of Some Unsymmetrical Configuration.—Three-center integrals which appear in this case have need of complicated calculations. However, it is possible that, by an analogy of Mulligan approximation for the unsymmetrical integrals with different z's, these integrals are expressed approximately in terms of symmetrical configurations.

For example, denoting $R_{AB}=R_1$ and $R_{BC}=R_2$, we have

$$(ab \mid bc)_{R_1,R_2} = (ab)_{R_1}\cdot(bc)_{R_2} \times\frac{1}{2}\left[\left(\frac{(ab \mid bc)}{(ab)(bc)}\right)_{R_1}+\left(\frac{(ab \mid bc)}{(ab)(bc)}\right)_{R_2}\right]$$

Otherwise, these integrals may be resolved into the sum of several two-center integrals by the use of Rudenberg-Mulliken type approximation. Calculation was carried out for the configurations of

$R_{AB}=1.5$ a. u., $R_{BC}=2.0$ a. u.
$R_{AB}=1.75$ a. u., $R_{BC}=2.0$ a. u.
$zR_{AB}=2.00$ a. u., $zR_{BC}=2.50$ a. u.
and $zR_{AB}=2.25$ a. u., $zR_{BC}=2.50$ a. u.

by the use of Heitler-London and Wang ($z=1.4$) type functions and of approximate values of integrals.

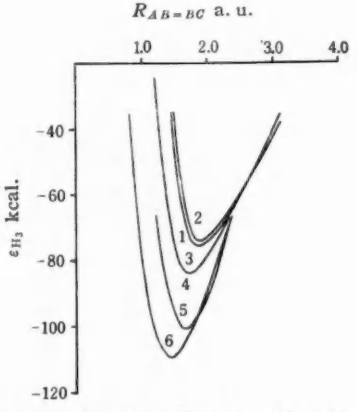

Fig. 1. Energies of symmetrical linea H_3.
1. Heitler-London function
2. H.-L.-plus-Ion function
3. Wang function (L.-H.)
4. Wang-plus-Ion function (L.-H.)
5. Wang function ($z=1.4$)
6. Observed H_2

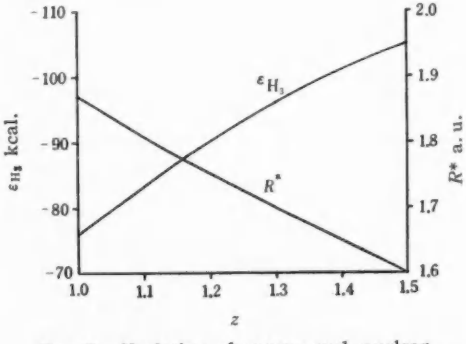

Fig. 2. Variation of energy and nuclear separation of H_3 with increase of z.

11) H. M. James, *J. Chem. Phys.*, **2**, 794 (1934).
12) J. F. Mulligan, ibid., **19**, 347 (1951).
13) S. Weinbaum, ibid., **1**, 593 (1933).

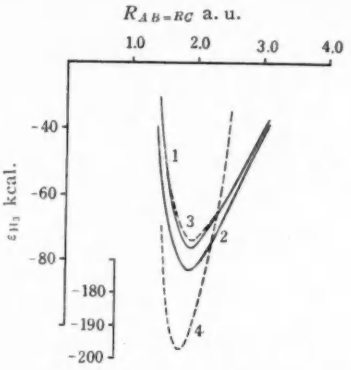

Fig. 3. Energies of H_3 by the use of various approximations.
1. Heitler-London function
2. Three-center integrals by R.-M. approximation
3. Neglect of three-center integrals
4. Neglect of three-center integrals and of non-orthogonality of atomic orbitals

TABLE III. VARIATION OF ENERGY BY BENDING*

(i) $R_{AB}=R_{BC}=2.00$ a. u. (Heitler-London type function)

ϕ (rad.)**	0.000	0.314	0.711
E (kcal.)	−81.8	−81.1	−77.4

(ii) $zR_{AB}=zR_{BC}=2.25$ a. u. (Wang type function $z=1.4$)

ϕ (rad.)	0.000	0.952
E (kcal.)	−100.1	−92.6

(iii) $zR_{AB}=zR_{BC}=2.50$ a. u. (Wang type function $z=1.4$)

ϕ (rad.)	0.000	0.902
E (kcal.)	−101.6	−95.7

* Values of three-center integrals with R.-M. approximation were used.
** ϕ is the angle between lines A-B and B-C.

TABLE IV. ENERGIES OF H_3 FOR UNSYMMETRICAL LINEAR CONFIGURATIONS*

	($z=1$)		($z=1.4$)	
zR_{AB} (a. u.)	1.50	1.75	2.00	2.25
zR_{BC} (a. u.)	2.00	2.00	2.50	2.50
E (kcal.)	−81.1	−83.7	−99.6	−103.4

* Values of three-center integrals with R.-M. approximation were used.

Results obtaind from calculations a)—h) are shown in Figs. 1—3 and Tables III and IV. An example of potential enegy surface constructed from these data is also shown in Fig. 4.

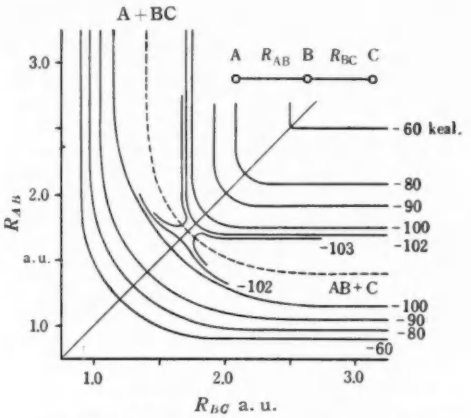

Fig. 4. Potential energy surface of reaction $H_2+H\rightarrow H+H_2$ (Wang type function $z=1.4$).

Discussion

Activation energies obtained by the present method (Table V) are not always satisfactory compared with the observed value[14] or the previous ones by Hirschfelder et al.[1], except the result with Wang

TABLE V. VALUES OF ENERGY OF H_3, E_{H_3}, NUCLEAR SEPARATION, R^*, AT ACTIVATED STATE AND OF ACTIVATION ENERGY, E_a, OBTAINED BY VARIOUS TREATMENTS

Used molecular function	(kcal.) E_{H_3}	E_{H_2}	E_a	(a. u.) R^*
Heitler-London	−76.0	−109.5	33.5	1.87
(R.-M. approx.)	−83.0	−109.5	26.5	1.87
(H.-E.-R.)*	−53.11	− 72.18	19.07	2.00
H.-L.-plus-Ion.	−75.0	−109.5	34.5	1.88
(H.-E.-R.)	−60.39	− 74.02	13.63	2.00
Wang.	−88.0	−109.5	21.5	1.77
(L.-H.)**	−84.0	−109.5	25.5	1.72
(H.-E.-R.)	−56.16	− 86.94	30.78	1.89
Wang-plus-Ion	−88.0	−109.5	21.5	1.73
(L.-H.)	−84.0	−109.5	25.5	1.72
(H.-E.-R)	−67.09	− 92.24	25.15	1.84
Wang. ($z=1.4$)	−101.0	−109.5	8.5	1.65
(R.-M. approx.)	−102.4	−109.5	7.1	1.72
Griffing et al.[3]***	−63.0	− 71.76	8.76	1.82
Kimball et al.[3]***	−72.4	—	—	1.93
Observed value[14]	—	−109.5	4∼8	—

* Values calculated by Hirschfelder, Eyring and Rosen.
** Values calculated by the use of Hirschfelder-Linnett's coefficients.
*** Values calculated by the LCAO-MO method with configuration interaction.

14) K. H. Gelb and P. Harteck, *Z. physik. Chem.* (*Bodenstein Festband*), 849(1931); A. Farkas and L. Farkas, *Proc. Roy. Soc.*, **A152**, 124 (1935).

type function in which $z=1.4$. However, marked improvements from their work are found in the absolute energy values of H_3 complex state, that is, the lowering 15~30 kcal. Besides, it is apparent that the activation energies estimated by them are of relative character; the use of improved function of H_2 brings, on the contrary, large increase for the values.

Interesting results are seen for the influence of an added ionic term. The introduction of this term lowers energies of H_3 complex slightly in the case of Hirschfelder et al., while it has almost no effect in the present treatment. These results are owing partly to the small contribution of ionic state to the lowest one and partly to the use of fixed coefficient of that term.

Also the results are explained phenomenally as that addition of this state brought an increase of interaction energy allowing superposition of electrons on the same atom. Considerations shall be done again later relating to the distribution of electrons in the system.

Next, the effect of nuclear charge z is examined. The lowering of energy and the contraction of the dimension of activated complex with increase of z are shown in Fig. 2. When z is increased to 1.4 or larger, the activation energy calculated attains the observed one. This effect may be explained qualitatively as that the use of atomic orbital shrunk by larger z diminishes the interaction between species and then energy of complex and nuclear distance decrease to those of the initial molecule.

If the energies of molecular species are estimated by the use of the same approximate function, this decrease of interaction energy will be compensated by the increase of molecular energy, and then an optimum value of z will be obtained. Accordingly, the variational principle does not always hold in the present method which makes use of the experimental value of molecular energy. However, this "half-theoretical" character of the present method gives an advantage of taking the nuclear charge z as an arbitrary parameter. According to this idea, it becomes possible to choose the z value from such a different point of view as will be discussed below.

When the atom C is separated infinitely from the molecule AB, the energy of the lowest state is apparently equal to that of molecule AB and that of the next higher state belonging to another doublet is expressed, by the use of Wang type function, as follows:

$$E_1=\frac{1}{R_{AB}}+\frac{Q-J}{1-S^2} \tag{8}$$

where

$$S=(ab) \tag{9}$$

$$Q=(a^2\mid b^2)-(a^2\mid B)-(b^2\mid A) \tag{10}$$

and

$$J=(ab\mid ab)-(ab)(ab\mid A+B) \tag{11}$$

This equation corresponds clearly to the theoretical expression of the repulsive ${}^3\Sigma_u^+$ state of H_2.

Since the energy of this state was evaluated accurately by James, Coolidge and Present[15] by the aid of the variation method, we can choose the parameter z so as to coincide the energy by Eq. 8 with the calculated value by them.

The result is satisfactory as shown in Fig. 5; when the nuclear distances R_{AB} and R_{BC} come near the configuration of activated state, z value approaches 1.4. This

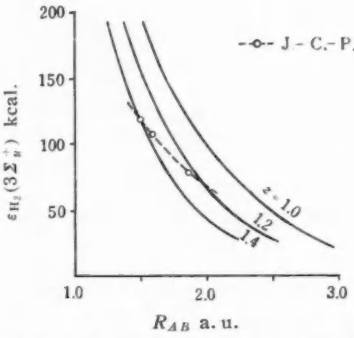

Fig. 5. Energy of triplet state of H_2.

fact suggests that the use of a composite function which gives better value for the energy of the state correlating strongly to the noticed one, improves the result markedly. Another qualitative reason of taking a larger value of z is in its effect upon the electronic distribution in the molecule. The present results will be improved if we make use of exact molecular function, e. g., James-Coolidge type one[16]. The distinction of J.-C. function from usual orbital ones is in its electronic distribution in which the overlapping of electrons is diminished by the introduction of inter-electronic coordinate r_{12}. This effect is

15) H. M. James, A. S. Coolidge and R. D. Present, *J. Chem. Phys.*, **4**, 187 (1936).
16) H. M. James and A. S. Coolidge, ibid., **1**, 825 (1933).

attained to some extent by the use of orbital functions with increasing z value. Also the addition of an ionic term, on the contrary, estranges the distribution from J.-C.'s. It is expected, therefore, that the utilization of larger z takes in partly the energy of electronic correlation in molecules, and then in the reacting system. It goes without saying that this correlation is partly included by the use of experimental data for the component species.

Potential Energy Basin

Here, the existence of so-called "potential energy basin" is briefly discussed.

By applying straightforwardly Eyring's semi-empirical method to the H_3 system of linear configuration, the obtained surface has two distinct basins[17], i.e., (a) a markedly deep one occurring where the distances between neighboring atoms, R_{AB} and R_{BC} are smaller than 1.0 a.u. and (b) a shallow one near the activated state.

Neither the results of the present calculation nor that of Hirschfelder et al.[1] show such basins as those above. The fact that these basins are apparent ones, being induced from the assumption of constant coulombic fraction, is explained as follows; for the shrunken configuration where both R_{AB} and R_{BC} are nearly equal to those giving zero bond energies, ε_{AB}, $\varepsilon_{BC}\simeq 0$, the coulombic and exchange parts of these bonds, Q_i and J_i $(i=AB, CB)$ are in the relation as

$$Q_i\simeq -J_i\gg 0 \tag{12}$$

while their values by Eyring's procedure are

$$(1-\rho)Q_1=\rho\cdot J_i\simeq 0 \tag{12'}$$

Therefore, the energy value which is obtained from London's formula,

$$E=Q_{AB}+Q_{BC}+Q_{CA}-[J_{AB}^2+J_{BC}^2+J_{CA}^2 -J_{AB}J_{BC}-J_{BC}J_{CA}-J_{CA}J_{AB}]^{1/2} \tag{13}$$

and these Q's and J's, is underestimated extremely as

$$E'=\varepsilon_{AC}=Q_{AC}+J_{AC} \tag{14'}$$

instead of exact value,

$$E=\varepsilon_{AC}+3Q_{AB}\gg E' \tag{14}$$

This situation is apparently the cause of basin a).

Next, the origin of basin b) is examined. For the equi-distant configuration "P" as shown in Fig. 7, the energy change ΔE, induced from the small displacements around P is expressed as

$$\Delta E_x\simeq\sqrt{2}\left[\left(\frac{\partial Q_{AB}}{\partial R_{AB}}\right)+\frac{1}{2}\left(\frac{\partial J_{AB}}{\partial R_{AB}}\right) +\left(\frac{\partial Q_{AC}}{\partial R_{AC}}\right)-\left(\frac{\partial J_{AC}}{\partial R_{AC}}\right)\right]\cdot(\Delta x) +\left[\frac{1}{2}\left(\frac{\partial^2 Q_{AB}}{\partial R_{AB}^2}\right)+\frac{1}{4}\left(\frac{\partial^2 J_{AB}}{\partial R_{AB}^2}\right) +\left(\frac{\partial^2 Q_{AC}}{\partial R_{AC}^2}\right)-\left(\frac{\partial^2 J_{AC}}{\partial R_{AC}^2}\right)\right]\cdot(\Delta x)^2 =A_1(\Delta x)+A_2(\Delta x)^2$$

along the x axis and

$$\Delta E_y\simeq\left[\frac{1}{2}\left(\frac{\partial^2 Q_{AB}}{\partial R_{AB}^2}\right)+\frac{1}{4}\left(\frac{\partial^2 J_{AB}}{\partial R_{AB}^2}\right) -\frac{3}{4}\cdot\frac{1}{|J_{AB}-J_{AC}|}\cdot\left(\frac{\partial J_{AB}}{\partial R_{AB}}\right)^2\right]\cdot(\Delta y)^2 =B_2(\Delta y)^2$$

along the y axis. According to Eyring's assumption of constant ρ, the minimum point appears at the position where the coefficient of (Δx), A_1, is equal to zero and the nuclear separation $R_{AB}^*(=R_{BC}^*)$ is slightly larger than the equilibrium distance r_e of H_2 (1.40 a.u.), for example, $R_{AB}^*=1.6$ and 1.9 a.u. for $\rho=0.2$ and 0.1, respectively. In the case of large coulombic fraction, therefore, this point is apparently in a basin, for $A_2>0$ and B_2, the coefficient of $(\Delta y)^2$, estimated approximately by the

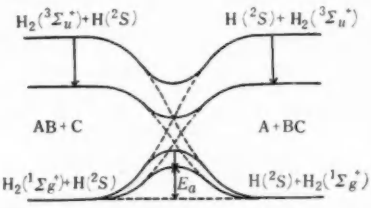

Fig. 6. Variation of activation energy with lowering of upper surface.

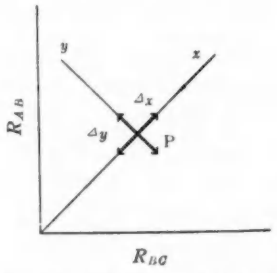

Fig. 7. Displacements around P.

17) S. Sato, This Bulletin, 28, 450 (1955).

use of equation

$$B_2 \simeq \frac{1}{4}\left(\frac{\partial^2 J_{AB}}{\partial R_{AB}^2}\right) - \frac{3}{4}\cdot\frac{1}{|J_{AB}-J_{AC}|}\cdot\left(\frac{\partial J_{AB}}{\partial R_{AB}}\right)^2$$

$$J_{AB} = (1-\rho)\cdot\varepsilon_{H_2}(R_{AB})$$

and of Morse function of H_2, is positive where

$$R_{AB}^* < 1.74 \text{ a. u.}$$

Alternatively, when we give up this assumption of constant ρ, the nuclear distances at the minimum point are somewhat extended. The value of B_2 estimated by making use of the following expression of J_{AB},

$$J_{AB} = D'\left[e^{-2a(r-r_e')} - 2e^{-a(r-r_e')}\right]^{18)}$$

where $D' = 0.9\, D_{H_2} = 98.51$ kcal./mol.

$r_e' = 0.9\, r_e = 1.261$ a. u.

and $a = 1.0298$,

is negative where

$$R_{AB}^* > 1.60 \text{ a. u.}$$

This result shows that the surface near the activated state is a saddle-like one or, at least, has not such a depression as was expected by Eyring et al.

Computation of Reaction Rate

Now, we shall evaluate the rate of the reaction on the knowledge of the surface derived here. Such a detailed calculation has been done only by Eyring et al.[19] According to the activated complex theory, the rate v and rate constant k of the elementary reaction $H_2(AB)+H(C)\rightarrow H(A)+H_2(BC)$ are expressed by

$$v = kC_{H_2}\cdot C_H \qquad (20)$$

and

$$k = \kappa\,\frac{I_{H_3}\sigma_{H_2}}{I_{H_2}\sigma_{H_3}}\cdot\frac{h^2}{(4\pi m_H/3)^{3/2}\cdot(kT)^{1/2}} \times\frac{1}{4}\cdot\frac{\sinh\left(\frac{1}{2}h\nu_{H_2}/kT\right)e^{-E_c/kT}}{\sinh\left(\frac{1}{2}h\nu_s/kT\right)\cdot\sinh^2\left(\frac{1}{2}h\nu_\phi/kT\right)} \qquad (21)$$

The notations in these equations are as follows:

C; concentration of species.
κ; the transmission coefficient.
I; a moment of inertia.
σ; symmetry number.
m_H; mass of hydrogen atom.
ν_{H_2}; vibrational frequency of H_2.
ν_s and ν_ϕ; stretching and bending vibrational frequencies of activated complex respectively.
E_c; classical energy of activation.

The quantities belonging to molecule or complex are distinguished by the addition of subscripts, e. g., "H_2" or "H_3". Since the complex in the present result is a symmetrical linear one, $\sigma_{H_2}=\sigma_{H_3}=2$ holds. Constants deduced from the surface constructed by the use of Wang type function ($z=1.4$) are shown in Table VI with Eyring's ones.

TABLE VI. CONSTANTS FOR THE HYDROGEN ATOM-MOLECULE REACTION

	Present result*	Eyring et al.**
R_{AB}^* (Å)	0.88 (0.91)	1.354
R_{BC}^* (Å)	0.88	0.753
I_{H_3} (10^{-40} gcm^2)	2.62	3.79
I_{H_2} (〃)	0.458	0.458
$1/2\cdot h\nu_s$ (kcal.)	4.78	5.18
$1/2\cdot h\nu_\phi$ (kcal.)	1.35	0.95
$1/2\cdot h\nu_{H_2}$ (kcal.)	6.27	6.21
E_c (kcal.)	8.5 (7.1)	7.63

* Values obtained by the use of Wang type function with $z=1.4$. In parentheses, those with R.-M. approximation are shown.
** Values obtained from Ref. 19. Coulombic fraction $\rho=0.20$.

TABLE VII. RATE CONSTANTS OF HYDROGEN ATOM-MOLECULE REACTION, k (cc. mol^{-1} sec^{-1})

Temperature °K	300	600	1000
Observed values	9.0×10^7	—	2.2×10^{12}
Present results a.	3.6×10^6	1.0×10^{10}	0.4×10^{12}
〃 b.*	3.9×10^7	3.5×10^{10}	0.7×10^{12}
Eyring et al.	7.3×10^7	7.3×10^{10}	1.5×10^{12}

* Values obtained by the use of constants in parentheses, Table VI.

The evaluated rate values are given in Table VII, with the observed ones by Geib and Harteck and Farkas et al.[14] and also with the calculated ones by Eyring et al. Although detailed comparison is rather difficult because of few experimental data, the agreement with the evaluated ones is reasonably good. The reason why Eyring's values are slightly large compared with the present ones is in the use of larger moment-of-inertia value of the complex deduced from its unsymmetrical form. Accordingly, when we give up the assumption of constant ρ, the moment-of-inertia and therefore rate

18) The corresponding coulombic fractions obtained from this function are 0.13, 0.18 and 0.20 at $R_{AB}=1.5$, 2.0 and 2.5 a. u., respectively.
19) H. Eyring et al., "The Theory of Rate Processes", McGraw-Hill Book Co. Inc., New York, (1941), p. 203.

also are reduced to those near the present ones.

Besides, it is necessary to use corrected values of transmission coefficient for this reaction consisting of light atoms in low temperatures.

Since it is known that the bending of the reaction path scarcely affects the extent of transmission at all, the evaluation of κ is confined to that through potential energy barrier[20]. Now taking Wigner's correction, $\kappa = 1 - \frac{1}{24}\left(\frac{h\nu_t}{kT}\right)^2$, where ν_t is the imaginary vibrational frequency of complex along the reaction path, we obtain κ's values to be 6.3, 2.3 and 1.5 at 300, 600 and 1000°K respectively from the value $ih\nu_t = 6.8$ kcal. The rate values are then corrected to

$$2.5\times10^{8},\ 8.1\times10^{10} \text{ and } 1.1\times10^{12}$$

at respective temperatures. Since Wigner's correction may give upper limit of κ, it is sure that the rate in lower temperatures were well improved.

Conculusion

The method of modified bond eigenfunction was applied to construct the potential energy surface of the hydrogen atom-molecule reaction. Also it was shown that the reaction rates estimated on this surface were in agreement with the observed ones.

In the calculation of surface, we took effective nuclear charge z in orbital function as an arbitrary parameter and showed the propriety of employing a larger z value than unity. Accordingly, it is to be noted that the functions of component species near the configuration of activated state are different from those of "free species" and that, by the use of these deformations, some parts of electronic correlation energy are taken into calculation.

Recently, Arai et al.[21] have developed, in the field of "molecular theory", the method of "deformed-atoms-in-molecules" which differs from the original Moffitt's method by taking deformed atomic orbitals in the molecule. Then, it may be said that the method by the present author corresponds to a further extension of theirs for the reacting system.

Although, the electronic correlation is considered partly in the above-mentioned manner, its full inclusion by the device of more valid approximation for wave function will be the important problem to be studied hereafter.

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Laboratory of Physical Chemistry
Tokyo Institute of Technology
Meguro-ku, Tokyo

20) I. Yasumori and K. Fueki, This Bulletin, **29**, 1 (1956). For the effect of curved reaction path, I. Yasumori, ibid., **32**, 913 (1959).

21) T. Arai, *J. Chem. Phys.*, **26**, 435, 451 (1957); T. Arai and M. Sakamoto, ibid., **28**, 32 (1958).

The Mannich Base of Troponoid and its Application. II. On 5-Bromomethyltropolone Derivative

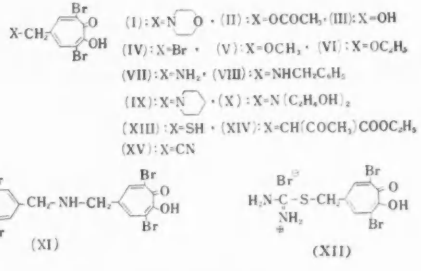
By Shuichi SETO and Kyozo OGURA

(Received March 26, 1959)

In the preceding paper[1], the authors reported on the derivation of 5-hydroxymethyl- and 5-formyltropolones from 3,7-dibromo-5-morpholinomethyltropolone, and on their reactions. In the present series of experiments, the 5-hydroxymethyl derivative was further led to 5-bromomethyl derivative and examination of this reaction showed some interesting results which are described herein.

Warming of 3,7-dibromo-5-hydroxymethyltropolone(III), obtained from 3,7-dibromo-5-morpholinomethyltropolone (I), in hydrobromic acid affords 3,7-dibromo-5-bromomethyltropolone(IV) as colorless needless, m. p. 140°C, in a good yield. IV is very reactive and reacts with various anionoid reagents to undergo substitution of bromine in the bromomethyl group as *p*-bromomethylphenol does[2].

Under some conditions, for example, treatment with sodium hydroxide solution, it forms a bis(tropolonyl)methane derivative. When IV is heated in methanol or ethanol, 5-methoxymethyl-(V) or 5-ethoxymethyltropolone derivative(VI) is obtained. These substances are the same as the compounds obtained on refluxing 5-acetoxymethyltropolone derivative(II) in methanol or ethanol. Reaction of IV with sodium acetate afforded II. Reaction with amines occurs easily at room temperature to afford the corresponding aminoalkyltropolone derivatives. Treatment with liquid ammonia, benzylamine, morpholine, piperidine and diethanolamine, respectively, affords 5-aminomethyl-(VII), 5-benzylaminomethyl-(VIII), 5-morpholinomethyl-(I), 5-piperidinomethyl-(IX), and 5-bis(β-hydroxyethyl)aminomethyltropolone (X) derivatives. I and IX are also obtained by the Mannich reaction of 3,7-dibromotropolone, and VII is also obtained in some cases by treatment of II with liquid ammonia. Reaction of IV with concentrated ammonium hydroxide gives bis(3,7-dibromotropolon-5-ylmethyl) amine (XI). All these aminoalkyltropolone derivatives form a water-soluble green iron complex with ferric chloride. IV undergoes reaction with thiourea in *tert*-butanol at room temperature to form *S*-(3,7-dibromotropolon-5-ylmethyl) isothiuronium bromide(XII) whose treatment with alkali affords 3,7-dibromo-5-mercaptomethyltropolone (XIII). IV forms a bis(tropolonyl)-methane derivative in strong alkali and its reaction with carbanions is not possible by the conventional method. Application of a large excess of the reagent to a dilute solution of IV gives the desired compound. For example, dropwise addition of a dilute solution of IV in ethyl acetoacetate with stirring, into a solution of a large excess of potassium compound of ethyl acetoacetate affords the anticipated 5-(β-acetyl-β-ethoxycarbonyl)tropolone derivative(XIV). Application of a large excess of potassium cyanide to a solution of IV in dioxane and water gives 5-cyanomethyltropolone derivative(XV).



Experimental[3]

3,7-Dibromo-5-bromomethyltropolone (IV). — A mixture of 2 g. of 3,7-dibromo-5-hydroxymethyltropolone(III) and 40 ml. of hydrobromic acid (sp. g., 1.38) was warmed for 15 min. and the colorless needle crystals that separated out were recrystallized from a benzene-cyclohexane mixture: m. p. 139~140°C. Yield, 2 g.

Anal. Found: C, 25.91; H, 1.89. Calcd. for $C_8H_5O_2Br_3$: C, 25.73; H, 1.34%. U. V. λ_{max}^{MeOH} mμ (log ε): 265(4.53), 350(4.21), 428(421).

1) S. Seto and K. Ogura, This Bulletin, **32**, 493 (1959).
2) K. Auwers, *Ber.*, **34**, 4264 (1901).
3) All melting points are not corrected.

3, 7-Dibromo-5-methoxymethyltropolone (V). — A solution of 10 mg. of IV in 1 ml. of methanol was heated on a water bath for about 10 minutes and the removal of methanol left colorless needles, m. p. 135°C, which showed no depression on admixture with the substance[1] obtained by refluxing II in methanol.

Anal. Found: C, 33.98; H, 2.73. Calcd. for $C_9H_8O_3Br_2$: C, 33.33; H, 2.47%. U. V. λ_{max}^{MeOH} mμ (log ε): 267(4.63), 346(4.29), 428(4.30).

3, 7-Dibromo-5-ethoxymethyltropolone (VI). — In exactly the same manner as in the cases of V and IV was heated in ethanol and colorless needles, m. p. 100°C, were obtained. These showed no depression on admixture with the substance[1] obtained by the refluxing of II in ethanol.

Anal. Found: C, 35.62; H, 2.91. Calcd. for $C_{10}H_{10}O_3Br_2$: 35.54; H, 2.96%.

3, 7-Dibromo-5-aminomethyltropolone (VII).—(a) A solution of 100 mg. of IV dissolved in ca. 5 ml. of liquid ammonia was allowed to stand at room temperature for 4 days. The yellowish brown residue which was obtained by removal of liquid ammonia was extracted with 1.5 N hydrochloric acid. The extract was neutralized to pH 2.5 and the precipitate thereby formed was collected. Washing of this precipitate with water and methanol afforded yellow powder, m. p. 225°C (decomp.).

b) A solution of 100 mg. of II dissolved in ca. 100 ml. of liquid ammonia was allowed to stand for a week. VII was obtained by treating the residue in the same manner as in the case of a).

Anal. Found: C, 29.62; H, 3.27; N, 4.04. Calcd. for $C_8H_7O_2NBr_2 \cdot H_2O$: C, 29.35; H, 2.75; N, 4.28%. U. V. λ_{max}^{MeOH} mμ (log ε): 268(4.44), 345 (3.95), 430(3.98).

3,7-Dibromo-5-benzylaminomethyltropolone(VIII). —About 30 mg. of IV was dissolved in one drop of benzylamine and the solution was warmed at 50°C for a few minutes. By this process yellow crystals separated out. About 1 ml. of acetic acid-water was added to this mixture, the crystals were collected by filtration, and recrystallized from ethanol; m. p. 180°C. Yield, ca. 30 mg.

Anal. Found: C, 43.94; H, 3.57; N, 3.10. Calcd. for $C_{15}H_{13}O_2NBr_2 \cdot 2H_2O$: C, 43.17; H, 3.59; N, 3.35%. U. V. λ_{max}^{MeOH} mμ (log ε): 267(4.32), 347 (3.95), 430(3.87).

3, 7-Dibromo-5-piperidinomethyltropolone (IX).— a) The addition of 0.5 ml. of piperidine to 50 mg. of IV resulted in excessive generation of heat and a solution was effected. Addition of water to this solution produced a yellow precipitate. This mixture was adjusted to pH 5 with hydrochloric acid, the precipitate was collected, and washed with water and ethanol. m. p. 189~190°C (decomp.). Yield, ca. 20 mg.

b) A mixture of 400 mg. of 3,7-dibromotropolone(I) in 0.6 ml. of acetic acid and 0.4 ml. of piperidine was heated at 100°C and when in solution, 0.2 ml. of formaldehyde solution (37%) was added dropwise, with stirring. After about 10 min. of stirring and heating, the yellow precipitate that formed was collected and washed with water and ethanol, m. p. 190°C (decomp.). Yield, 490 mg. This substance showed no depression of melting point on admixture with the substance obtained by method a).

Anal. Found: C, 41.69; H, 3.95; N, 3.74. Calcd. for $C_{13}H_{15}O_2NBr_2$: C, 41.38; H, 3.98; N, 3.72%. U. V. λ_{max}^{MeOH} mμ (log ε): 268(4.02), 350 (3.71), 425(3.71).

3, 7-Dibromo-5-bis(β-hydroxyethyl)aminomethyltropolone (X). — A solution of 30 mg. of IV dissolved in 3 drops of diethanolamine was neutralized with 2 N hydrochloric acid and the yellow precipitate that formed was collected, washed with water and methanol; m. p. 160°C.

Anal. Found: C, 35.60; H, 3.89; N, 3.69. Calcd. for $C_{12}H_{15}O_4NBr_2$: C, 36.27; H, 3.78; N, 3.52%. U. V. λ_{max}^{MeOH} mμ (log ε): 267(4.21), 350 (3.90), 430(3.87).

Bis(3, 7-dibromotropolon-5-ylmethyl)amine (XI). —A mixture of ca. 30 mg. of IV in 0.5 ml. of concentrated ammonium hydroxide was stirred for a few minutes at room temperature. By this process yellow crystals precipitated out. This mixture was neutralized with 2 N hydrochloric acid, the yellow powder so formed was collected, and washed with water and methanol; m. p. 196°C.

Anal. Found: C, 31.31; H, 1.98; N, 2.59. Calcd. for $C_{16}H_{11}O_4NBr_4$: C, 31.94; H, 1.83; N, 2.31%. U. V. λ_{max}^{MeOH} mμ (log ε): 268(4.40), 345 (4.06), 425(4.00).

S-(3,7-Dibromotropolon-5-ylmethyl)isothiuronium Bromide (XII).—A solution of 40 mg. of IV and 20 mg. of thiourea dissolved in 3 ml. of *tert*-butanol was stirred at room temperature for a few minutes and the colorless crystals that separated out were collected, and washed with ethanol; m. p. 223~224°C (decomp.). Yield, 50 mg.

Anal. Found: C, 24.59; H, 2.42; N, 6.51. Calcd. for $C_9H_9O_2N_2SBr_3$: C, 24.05; H, 2.00; N, 6.24%. U. V. λ_{max}^{MeOH} mμ (log ε): 268(4.59), 335 (3.88), 387(3.71), 420(3.58).

3, 7-Dibromo-5-mercaptomethyltropolone (XIII). —A mixture of 50 mg. of XII in 0.5 mol. of 45% sodium hydroxide solution was heated for a few minutes on a water bath and neutralized by pouring this mixture into 6 N hydrochloric acid containing cracked ice. The precipitate that formed was collected and recrystallized from ethanol to give pale yellow needles, m. p. 128°C. Yield, 20 mg.

Anal. Found: C, 30.10; H, 1.84. Calcd. for $C_8H_6O_2Br_2S$: C, 29.45; H, 1.82%. U. V. λ_{max}^{MeOH} mμ (log ε): 267(4.46), 350(4.01), 430(3.86).

3, 7-Dibromo-5-(β-acetyl-β-ethoxycarbonylethyl)-tropolone (XIV). — A solution of 500 mg. of IV dissolved in 50 ml. of ethyl acetoacetate was added dropwise into a solution of 1 g. of potassium dissolved in 50 ml. of ethyl acetoacetate, with stirring at room temperature. The solution was further stirred for 2 hr. at room temperature,

neutralized with 6 N sulfuric acid to pH 5, and the ethyl acetoacetate layer was separated. The acetate layer was washed with water and evaporated under reduced pressure to remove the acetate. The dark red, oily residue crystallized on addition of ether, the crystals were collected, washed with ether, and recrystallized from a mixture of benzene and petroleum ether; m. p. 114~115°C. Yield, 350 mg.

Anal. Found: C, 39.83; H, 3.74. Calcd. for $C_{14}H_{14}O_5Br_2$: C, 39.81; H, 3.32%. U. V. λ_{max}^{MeOH} mμ (log ε): 268(4.55), 345(4.07), 430(3.96).

3, 7-Dibromo-5-cyanomethyltropolone (XV). — A solution of 150 mg. of IV dissolved in 3 ml. of dioxane was added dropwise, with stirring, into a solution of 150 mg. of potassium cyanide dissolved in 6 ml. of dioxane and 1 ml. of water at room temperature, the drops causing a transitory red color to appear. After completion of addition, the mixture was stirred for 1 hr., the solvent was removed under reduced pressure at room temperature, and the residue was acidified with hydrochloric acid. The brown precipitate that formed was collected and recrystallized from benzene; m. p. 148~151°C. Yield, 100 mg. During recrystallization, bis(3,7-dibromotropolon-5-yl)-methane formed as a benzene-insoluble by-product.

Anal. Found: C, 34.04; H, 1.80; N, 3.82. Calcd. for $C_9H_5O_2NBr_2$: C, 33.86; H, 1.57; N, 4.39%. U. V. λ_{max}^{MeOH} mμ (log ε): 267(4.50), 345(4.04), 430(3.98).

Summary

Reaction of 3,7-dibromo-5-hydroxymethyltropolone with hydrobromic acid affords 3, 7-dibromo-5-bromomethyltropolone, which has a high reactivity and reacts with various anionoid reagents to undergo substitution of bromine in the bromomethyl group. In this manner it is possible to extend the substituent by forming C–O, C–N, C–S and C–C bonding at the tip of the methyl group in position 5 of the tropolone ring.

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The Chemical Research Institute of Non-Aqueous Solutions
Tohoku University
Katahira-cho, Sendai

Synthesis of Polyanhydride. I. Mixed Anhydride of Aromatic and Aliphatic Dibasic Acids*

By Naoya YODA and Akihisa MIYAKE

(Received February 4, 1959)

The polyanhydride of aromatic dibasic acid was first prepared by Bucher and Slade[1], who reported that the crystalline polymer of the melting point above 300°C was obtained by heating isophthalic acid or terephthalic acid with acetic anhydride. Aliphatic polyanhydride was synthesized in 1932 by Hill and Carothers[2] who have investigated the preparation of polyanhydride from sebacic acid. Although possessing fiber-forming properties, it was reported that the aliphatic polyanhydride melted at too low a point to be of practical interest and the polymer gradually disintegrated in the presence of moisture due to hydrolytic degradation. On account of these unfavorable properties, the study of polyanhydride has not been taken into consideration since then. In 1957, however, Conix[3] reported that aromatic polyanhydride prepared from di-(*p*-carboxyphenoxy)-α, ω-alkane has shown excellent film and fiber-forming properties. This might be ascribed to the hydrophobic nature of polymer molecules, caused by the accumulation of phenylene nuclei along the polymer chain to form a regular molecular structure very closely packed as observed in polyethylene terephthalate.

The present investigation has been undertaken in order to study the synthesis

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1) J. E. Bucher and W. C. Slade, *J. Am. Chem. Soc.*, **32**, 1319 (1909).

2) J. W. Hill and W. H. Carothers, ibid., **54**, 1569 (1932).

3) A. Conix, *Makromol. Chem.*, **24**, (1) 76 (1957); *J. Polymer Sci.*, **29**, 343 (1958).

of mixed polyanhydrides of aromatic and aliphatic dibasic acids. As described herein, the mixed polyanhydrides of random structure were obtained when the calculated amount of aromatic and aliphatic dibasic acids had been mixed and treated with acetic anhydride which caused them to polymerize by heating in vacus. When suitable amounts of aromatic and aliphatic dibasic acids were used, it was possible to obtain mixed polyanhydrides of practical interest having their melting points in the range of 200 to 250°C. Using terephthalic acid as aromatic dibasic acid and adipic acid or sebacic acid as aliphatic dibasic acid, the mixed dibasic acids can be transformed into mixed anhydride with acetic anhydride. These mixed anhydrides polymerize by splitting off acetic anhydride. The diagram of composition versus melting point was obtained. From this the composition of mixed polyanhydride having its melting point in the range of 200°C to 250°C has been obtained for terephthalic acid-adipic acid, and terephthalic acid-sebacic acid copolymers.

Furthermore, the preparation of aromatic and aliphatic mixed polyanhydrides of regular structure have been investigated by the polycondensation reaction of diacid halide with dibasic acid in organic solvent pairs such as pyridine-benzene and pyridine-ether. The mixed polyanhydrides of regular structure having their melting points at 225°C (adipic acid) and 215°C (sebacic acid) have been synthesized, and the influence of chemical structure on the physical properties of these polymers was discussed[4].

Experimental and Results

Materials.—Commercially available sebacic acid and adipic acid were recrystallized from ethanol. The melting point was 133°C and 151~153°C, respectively. The purified terephthalic acid was obtained by converting it into dimethyl ester, followed by vacuum distillation and alkaline hydrolysis. Thus, carefully purified aliphatic and aromatic dibasic acids were used as a starting material for each polymerization.

Mixed Polyanhydride of Random Structure.—The mixed polyanhydride of terephthalic acid and adipic acid was obtained by polycondensation reaction using the excess of acetic anhydride. The detailed procedure is described as follows.

A 13.3 g. (0.08 mol.) portion of terephthalic acid and 17.5 g. (0.12 mol.) of adipic acid were mixed together and 415 ml. of acetic anhydride (b. p. 130°C) were added to the mixture. The combined solution was refluxed on an oil bath at 150~160°C for 8 hr. After the dibasic acids were completely dissolved into acetic anhydride, reflux was continued for an additional one hour and the excess of acetic anhydride was distilled off under water jet pump pressure to form mixed anhydride of low melting crystalline solid. The prepolymer thus formed was heated under dry nitrogen atmos phere in vacuo at 240°C for 1.5 hr. The resulting polyanhydride has its melting point at 235°C and possesses fiber-forming property. The intrinsic viscosity of polymer measured in 1,4-dioxane at 30°C was 0.130. However, it becomes brittle shortly after spinning due to its hydrolytic degradation by absorbing moisture. When purified terephthalic acid and adipic acid were used, it was possible to avoid coloration by impurities on heating.

The relationship between the melting point and the composition of terephalic acid and adipic acid was measured and its mole fraction was plotted against the melting point of copolymer as shown in Fig. 1. It gives the minimum melting point at 47~48°C where the composition of copolymer

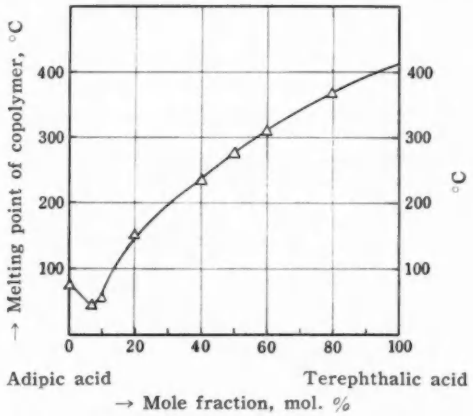


Fig. 1. Relation between composition and melting point of adipic acid-terephthalic acid anhydride copolymer.

is 93 mol. % of adipic acid. Polyanhydride of terephthalic acid itself has its melting point above 410°C. Two acids, e. g., terephthalic acid and aliphatic acid, furnish a series of copolymers in which the melting point and degree of crystallinity increase as the proportion of terephthalic acid is increased over 10 mol. %.

The experimental results are summarized in Table 1. The infrared spectrum of the polymerization product has absorption bands of anhydride carbonyl group at 5.56 and 5.78 μ as illustrated in Fig. 2[5].

The polycondensation proceeds smoothly upon heating in vacuo to obtain a linear polymer and

4) N. Yoda, *Makromol. Chem.* **32**, (1) 1 (1959).

5) L. J. Bellamy, "The Infrared Spectra of Complex Molecules", 2nd. Ed., Methuen & Co., London (1958), p. 127—129.

TABLE I. COMPOSITION AND MELTING POINT OF TEREPHTHALIC ACID-ADIPIC ACID ANHYDRIDE COPOLYMERS

Expt. No.	Terephthalic acid mol. %	Adipic acid mol. %	m. p., °C	Properties	$[\eta]^{30°C}_{1,4\text{-Dioxane}}$
1	0	100	75～ 77	Crystallizes readily	—
2	7	93	47～ 48	Crystallizes readily	—
3	10	90	53～ 55	Crystallizes readily	—
4	20	80	150～155	Crystallizes, fiber-forming	0.116
5	40	60	235	Crystallizes, fiber-forming	0.130
6	50	50	275	Crystalline solid	—
7	60	40	310	Crystalline solid	—
8	80	20	365	Crystalline solid	—

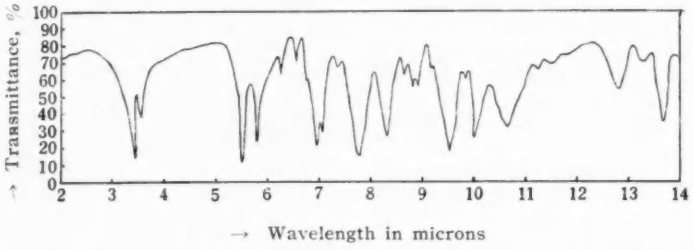


Fig. 2. The infrared spectrum of polyanhydride of adipic acid-terephthalic acid system (KBr)

the infrared data support the fact that the chains link with each other by anhydride groups and are terminated by acetyl groups derived from the reagent used in bringing about the anhydride formation.

The polymerization is started even by simple heating at 220～250°C at atmospheric pressure. A much faster reaction, leading to the formation of polyanhydride of higher molecular weights is observed, however, on heating the mixed anhydrides in vacuo under dry nitrogen atmosphere at elevated temperatures in order to facilitate the removal of acetic anhydride.

In the same manner, the mixed polyanhydride of terephthalic acid and sebacic acid was prepared by polycondensation of purified sebacic acid and terephthalic acid. The detailed procedure is illustrated below.

A 17 g. portion (0.10 mol.) of terephthalic acid and 40 g. (0.20 mol.) of sebacic acid were pulverized and 1000 ml. of acetic anhydride was added to the mixture. The solution was refluxed at 150～160°C for 8 hr. After distilling off the excess of acetic anhydride, a mixed anhydride of low melting crystalline solid was obtained. The prepolymer was heated under dry nitrogen atmosphere in vacuo at 230°C for 1.5 hr. to form polyanhydride having its melting poing at 220°C. This possesses a fiber-forming property and it is somewhat elastic. It becomes brittle shortly after spinning due to its hydrolytic degradation by absorbing moisture. The intrinsic viscosity of polymer measured in *p*-dioxane at 30°C immediately after spinning was 0.162.

The relationship between the melting point versus the composition of terephthalic acid and

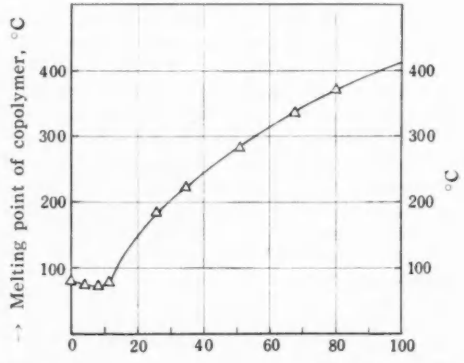


Fig. 3. Relation between composition and melting point of sebacic acid-terephthalic acid anhydride copolymer.

sebacic acid was obtained and its mole fraction was plotted against the melting point of copolymer as shown in Fig. 3. It was found that the minimum melting point was at 75°C where the composition of copolymer was 95.6 mol. % of sebacic acid and 4.4 mol. % of terephthalic acid. The experimental results are summarized in Table II. The infrared spectrum of copolymer has carbonyl absorption bands at 5.56 and 5.78 μ as shown in Fig. 4[5].

Infrared spectra indicate that polyanhydride before hydrolysis has two carbonyl absorption

TABLE II. COMPOSITION AND MELTING POINT OF TEREPHTHALIC ACID-SEBACIC ACID ANHYDRIDE COPOLYMERS

Expt. No.	Terephthalic acid mol. %	Sebacic acid mol. %	m. p., °C	Properties	$[\eta]_{1,4\text{-Dioxane}}^{30°C}$
1	0	100	79~80	Crystallizes readily	—
2	4.4	95.6	78	Crystallizes readily	—
3	8.5	91.5	75	Crystallizes readily	—
4	11.0	89.0	80	Crystallizes readily	—
5	25.9	74.1	185	Crystallizes, fiber-forming	0.081
6	34.4	65.6	220	Crystallizes, fiber-forming	0.162
7	51.1	48.9	280	Crystalline solid	—
8	67.7	32.3	335	Crystalline solid	—
9	80.7	19.3	370	Crystalline solid	—

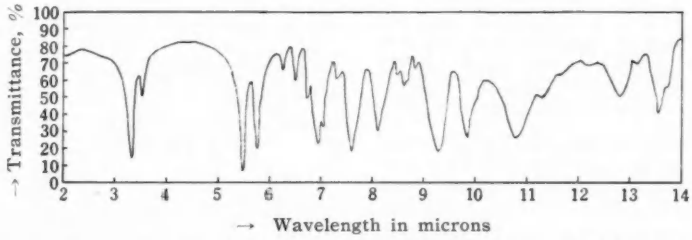


Fig. 4. The infrared spectrum of polyanhydride of sebacic acid-terephthalic acid system (KBr)

bands of the anhydride group at 5.56 and 5.78 μ. In addition to the carbonyl absorptions, the anhydride group also shows a strong band due to the C-O-C stretching vibration at 9.56 μ. When the polymer is exposed to moisture, the carbonyl absorption band at 5.86 to 5.95 μ appears. This indicates the existence of aliphatic and aromatic carboxylic acid carbonyl groups. The absorption bands at 3.71 and 3.95 μ are also observed. These can be taken as a strong evidence for the presence of dimeric carboxylic acid by taking account of bands existing in the carbonyl region.

When polyanhydrides of random structure are exposed to alkaline solution, it leads to the complete hydrolysis of anhydride to form aromatic and aliphatic dicarboxylic acids. An infrared spectrum shows neither anhydride carbonyl bands at 5.56 and 5.78 μ nor an ether band at 9.56 μ. On the contrary, the typical carboxylic acid bands appear at 3.71 and 3.95 μ of dimeric carboxylic acid bands and the strong carbonyl band at 5.86 μ[5].

The mixed anhydride of three components of dibasic acid such as the terephthalic acid, the adipic acid and the sebacic acid system was prepared by polycondensation reaction using the excess of acetic anhydride. The polymerization procedure is described as follows.

A 8.3 g. portion (0.05 mol.) of terephthalic acid, 7.3 g. of adipic acid (0.05 mol.) and 10.1 g. (0.05 mol.) of sebacic acid were thoroughly mixed in a mortar and refluxed with 550 ml. of acetic anhydride at 150~160°C for 8 hr. After all the acids were completely dissolved into acetic anhydride, the excess of acetic anhydride was distilled off under reduced pressure to form a mixed anhydride which was a low-melting crystalline solid. Then the prepolymer was heated under dry nitrogen atmosphere in vacuo at 250°C for 1.5 hr. to form a polyanhydride having a melting point at 245°C, which possesses a fiber-forming property.

Polymerization with acetyl chloride was also studied for dibasic acid anhydride of terephthalic acid and adipic acid or sebacic acid. In this case, the fiber-forming copolymer having a melting point at 210~230°C was also obtained with the mole fraction of 40 mol. % of terephthalic acid and 60 mol. % of adipic acid or sebacic acid.

Mixed Polyanhydride of Regular Structure.— Attempting to prepare the polyanhydride in which aromatic dibasic acid and aliphatic dibasic acid link with each other in a regularly bonded form, the polycondensation reaction of dibasic acid and dibasic acid chloride by dehydrochorination was studied in organic solvent pairs such as pyridine-ether, pyridine-benzene and dimethyl formamide-dimethyl aniline. Furthermore, the reaction of dibasic acid chloride with dimethyl ester of dibasic acid was investigated. In this case, terephthalic acid was again used for aromatic dibasic acid, and adipic acid or sebacic acid was chosen for aliphatic dibasic acid.

Preparation of Dibasic Acid Chloride.— Terephthalic acid chloride was prepared by the action of phosphorus pentachloride on terephthalic acid. After extraction with ether, it was dried over anhydrous sodium sulfate and the ether was evaporated off. The recrystallizations from ligroin after decolorization with activated charcoal

gave colorless needles, m.p. 83.0°C (yield, 67%).

Adipic acid chloride was also obtained by refluxing adipic acid with the excess of thionyl chloride on a water bath for 4 hr. After evaporating off the excess of thionyl chloride, it gave adipic acid chloride which boiled at 112~115°C/10 mmHg (yield, 60%). Sebacic acid chloride was prepared in the same manner mentioned above with thionyl chloride to obtain a product boiling at 161°C/14 mmHg (yield, 45%). In order to avoid hydrolysis, the solvents used for the polymerization were carefully purified each time before use. Pyridine (C. P. grade) was refluxed with barium oxide and distilled, and the fraction at 115.5°C was taken. Benzene and ether were dried over metallic sodium and distilled immediately before use.

Polymerization in Pyridine-Ether Medium —A 4.5 g. portion (0.03 mol.) of terephthalic acid was dissolved into 120 ml. of pyridine and 5 g. (0.03 mol.) of adipic acid chloride dissolved into 100 ml. of ether were added dropwise into the reaction system with ice cooling under dry nitrogen atmosphere.

When acid chloride is added into pyridine, the pyridine complex is formed[6]. The reaction temperature was gradually raised to 25~30°C and stirring was continued for 4 hr. at this temperature. The resulting polymer was filtered, washed and dried to obtain polyanhydride having a melting point at 250°C. The existence of the anhydride group was confirmed by the infrared spectrum which showed acid anhydride absorption bands in a carbonyl region[5].

Polyanhydride of sebacic acid-terephthalic acid obtained under the same reaction condition has its melting point at 240°C, and the infrared spectrum has acid anhydride absorption bands in a carbonyl region[5].

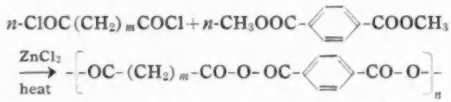
On the contrary, polyanhydride of terephthalic acid chloride and aliphatic acid forms a white crystalline solid, melting at 300°C with decomposition. The infrared spectrum shows acid anhydride and carboxylic acid absorption bands in a carbonyl region.

Polymerization in Pyridine-Benzene Medium.— When a pyridine-benzene solvent pair is used for the dehydrochlorination of terephthalic acid and aliphatic dibasic acid chloride, it was observed that the reaction proceeded more smoothly than in a pyridine-ether medium to form a white crystalline solid having its melting point at 225°C. The infrared spectrum shows carbonyl absorption band at 5.50 and 5.70 μ.

The reaction of sebacic acid chloride and terephthalic acid was also studied under the same reaction conditions, and white crystalline polymer melting at 215°C was obtained. The percent conversion of polyanhydrides in pyridine-benzene was found to be higher than that of polyanhydrides in pyridine-ether. The infrared spectrum indicates the existence of the acid anhydride group in a carbonyl region.

Polymerization of Dibasic Acid Chloride with Dibasic Acid Methyl Ester in the Presence of Zinc Chloride Catalyst.—As one of the processes to prepare polyanhydrides of regular structure, the polymerization reaction of dibasic acid chloride with dibasic acid methyl ester in the presence of zinc chloride was studied. The polyanhydrides of regular structure having their melting points at 203°C (adipic acid-terephthalic acid) and at 195°C (sebacic acid-terephthalic acid) were obtained.

Kyrides and Dvornikoff[7] reported the reaction of dialkyl phthalate and phthalyl chloride to give anhydride and the alkyl chloride. The improved method of the reaction of diacid chloride and diacid ester was employed in the presence of zinc chloride as a catalyst. The following reaction takes place for the polymerization in this case.



$m = 4$ or 8

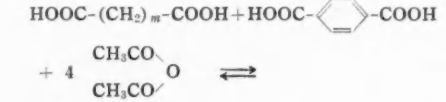
Although it is relatively stable against hydrolytic degradation, coloration of the polymer was observed when it was heated above 200°C.

In the same manner, polyanhydride obtained from sebacic acid chloride melts at 195°C and coloration occurs when it is heated above 200°C. It was found that the polymer thus obtained was relatively stable towards hydrolysis and it has a melting point with thermal decomposition. The polycondensation in dimethyl formamide medium was also studied and the polymers thus obtained failed to show good hydrolytic and thermal stability. It was found from the experimental results obtained above that the dehydrochlorination reaction of acid chloride and dibasic acid in pyridine-benzene medium gave the most satisfactory results.

Infrared Absorption Measurements. — The spectra were recorded with a Perkin-Elmer Model 21 spectrophotometer using an NaCl prism. Potassium bromide disks were used. The die and handpress were those supplied by the Shimadzu Co., Ltd.

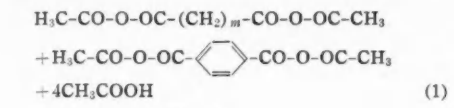
Discussion

The polycondensation reaction of aromatic and aliphatic dibasic acids with acetic anhydride proceeds through the following equations; firstly, the dibasic acids are converted into mixed anhydrides with acetic anhydride as shown in Eq. 1.



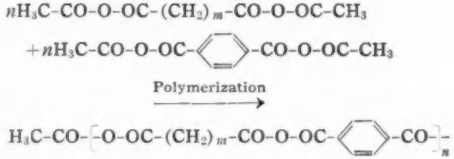
6) E. C. Harning, "Organic Syntheses", Col. Vol. III, John Wiley & Sons, Inc., New York (1955), p. 28.

7) L. P. Kyrides and M. N. Dvornikoff, *J. Am. Chem. Soc.*, **55**, 4630 (1933).



(1)

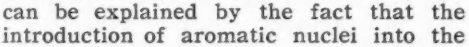
Secondly, these mixed anhydrides thus formed, which bear terminal acetyl end-groups and are low-melting crystalline solids, polymerize upon heating by splitting off acetic anhydride to form polyanhydride with high molecular weights as indicated in the following Eq. 2.



(2)

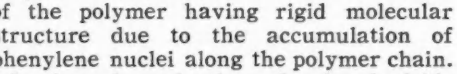
As to the mixed polyanhydride of random structure from aliphatic and aromatic dibasic acids, it was observed that the melting point and the degree of crystallinity increase with an increase in the proportion of aromatic dibasic acid. Presumably this can be explained by the fact that the introduction of aromatic nuclei into the polymer chain results in the formation of the polymer having rigid molecular structure due to the accumulation of phenylene nuclei along the polymer chain.

In the polymerization of polyanhydride of regular structure in pyridine-ether and pyridine-benzene media, the pyridine complexes of diacid chloride are first formed as shown in the following scheme:

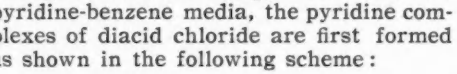


(3)

The pyridine complexes thus formed react with dibasic acid to obtain polyanhydride of regular structure as follows:

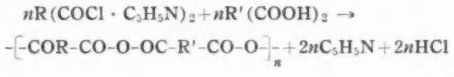


(4)



There are possibilities that anhydride interchange reaction takes place during the dehydrochlorination process at an elevated temperature to be transformed into the polyanhydride of random structure. This can be avoided, however, when the polymerization is performed at room temperature or at slightly elevated temperature under atmospheric pressure.

It is reasonably presumed that acid anhydride groups in a less closely packed polymer chain (e. g., polyanhydride of random structure) are easily hydrolyzed in the presence of moisture[8], and the polyanhydride chain is disintegrated into low molecular weight dicarboxylic acid, as shown below:



(5)

The authors have further given their attention to the application of interfacial polycondensation[9] for the polymerization of polyanhydride, which involves a similar concept already mentioned in the case of polymerization in solvent pairs, using diacid chloride for one component in such organic solvent as chloroform or benzene, and sodium or potassium salt of dibasic acid or dimethyl ester of dibasic acid for another in aqueous alcohol phase at room temperature under nitrogen atmosphere[10]. Much room is left for the detailed study of polyanhydride synthesis in this field, and further investigation is necessary before it can be applied for general purposes.

Summary

Copolymerization reactions of mixed anhydrides of aliphatic and aromatic dibasic acids have been investigated. It has been shown that a polyanhydride of regular structure was obtained from diacid chlorides and dibasic acids in organic medium, and that polyanhydrides of random structure were obtained from the mixed aromatic and aliphatic dibasic acids. A polyanhydride having its melting point at 225°C was prepared for terephthalic acid and adipic acid copolymer of regularly linked structure and that having its melting point at 215°C for terephthalic acid and sebacic acid copolymer. It was found that the stability of copolymer towards hydrolytic and thermal degradations was greater for those with regularly

8) C. K. Ingold, "Structure and Mechanism In Organic Chemistry" Cornell Univ. Press, Ithaca, New York (1953), p. 754.

9) E. L. Wittbecker and P. W. Morgan, Abstracts of the 134th Am. Chem. Soc. Meeting, Chicago, Illinois. (September, 1958), p. 8T—12T.

10) N. Yoda, unpublished work.

linked structure than for a polyanhydride of random structure. The mixed polyanhydrides of random structure were prepared and the diagram of composition versus melting point was obtained. The mole fractions of the two acid components were found to be 35~40 mol. % of terephthalic acid and 60~65 mol. % of aliphatic dibasic acid for copolymers melting at 220 to 240°C. It has further been shown that aliphatic and aromatic dibasic acids furnish a series of copolymers in which the solubility decreases and the melting point and the degree of crystallinity increase as the proportion of aromatic dibasic acid is increased.

The authors wish to express their gratitude to Dr. K. Hoshino, the Director of the Research Department, and Dr. M. Watanabe for their interest in this research and the permission for its publication. Sincere thanks are also due to Professor Y. Ishii of Nagoya University for helpful discussion. The authors are indebted to Messrs. S. Tanaka and Y. Bamba for their cooperation in carrying out the experiments.

Central Research Laboratories
Research Department
Toyo Rayon Co., Ltd.
Otsu, Shiga

The Isolation of Technetium by Coprecipitation or Anion Exchange

By Fujio ICHIKAWA

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1. Coprecipitation of Technetium with Molybdate. — Technetium-99 having a long half-life is usually separated from fission products of uranium-235 after a long irradiation and cooling time. But technetium-99m is easily prepared as a decay product of molybdenum-99 from neutron irradiated molybdenum. Articles[1-3] on the coprecipitation of technetium mainly refer to that with sulfide, perrhenate and perchlorate. In this paper, the coprecipitation behavior in connection with the separation of technetium from molybdenum is reported.

Experimental. — Technetium-99m is not a β emitter but a γ emitter, whereas molybdenum-99 is a β and γ emitter. Accordingly the γ-ray spectrum peak of technetium-99m (0.140 MeV.) is measured with 256 channel pulse height analyzer, whereas molybdenum-99 is simply determined by measurement of β-ray activity with G-M counter.

Fifty milligrams of ammonium molybdate is irradiated in a J. R. R.-1 Reactor for 2 hr. at a flux of 10^{11} neutrons/cm^2/sec. Since the half-life of molybdenum-99 is 67 hr. and that of technetium-99m is 6.04 hr., radioactive equilibrium is reached after 23.08 hr. The irradiated sample is dissolved in 10 ml. of water after a day.

Two milliliters each of various precipitants is added to 1 ml. portion of this sample solution. A 5% solution of lead nitrate, calcium chloride, barium chloride, silver nitrate or uranyl nitrate is used as the precipitant. When calcium chloride is used, 1 ml. of 3 M aqueous ammonia is required for the complete precipitation of calcium molybdate. The precipitate formed is separated

TABLE I-1. COPRECIPITATION RATIO OF TECHNETIUM-99 m WITH SOME MOLYBDATES

Form of precipitate	Precipitation ratio of Mo-99 %	Precipitation ratio of Tc-99m %
$PbMoO_4$	99.2	99.6
	96.0	99.6
	86.4	87.5
$CaMoO_4$	94.4	23.1
	93.3	12.3
	96.5	20.1
	97.7	33.7
$BaMoO_4$	96.3	10.9
	94.7	41.4
	75.1	39.6
Ag_2MoO_4	85.5	51.6
	95.9	67.8
	96.7	41.8
UO_2MoO_4	85.0	35.2

1) J. B. Gerlit; "International Conference on the Peaceful Uses of Atomic Energy", Vol. 7, United Nations Publication, New York (1955), p. 145.
2) G. W. Parker, J. Reed and J. W. Ruch, AECD-2043.
3) N. Matsuura, M. Kojima and A. Iguchi, *Japan Analyst* (*Bunseki Kagaku*), **7**, 792 (1958).

from the supernatant solution by the aid of a centrifuge, a filter tube or an usual filtering funnel. The β and γ-ray activities of precipitates and supernatant solutions are measured by comparing them with the activities of the sample solution to which no precipitant was added. The separation ratio is calculated from those data and is shown in Table I-1.

Results. — A 99.6% portion of technetium-99m is coprecipitated with lead molybdate. About 70% of technetium-99m remains in the solution after calcium molybdate is precipitated, but a few per cent of molybdenum also remains by single precipitation. Seventy per cent of technetium-99m is not precipitated with barium molybdate or uranyl molybdate. J. A. Swartout[4] used silver molybdate in order to isolate technetium from molybdenum, but in the present study 50~60% of technetium is coprecipitated with silver molybdate.

The results mentioned above, are applied in two ways. One is an easy preparation of technetium-99m solution from irradiated calcium molybdate, and the other is an isolation of technetium-99m and molybdenum-99 from fission products by coprecipitation with lead molybdate.

(1) Fifty milligrams of calcium molybdate irradiated in J. R. R.-1 Reactor for 2 hr. is washed on a Toyo 5B filter paper with 10 ml. of water or 1% ammonium hydroxide and the β and γ activities of washings are measured. The results are shown in Table I-2.

The absorption curve of β-ray shows that calcium-45 coexists in the washings. This solution is passed through a cation-exchange column and almost all of the β contaminations are removed by this treatment.

TABLE I-2. SEPARATION OF TECHNETIUM-99m FROM IRRADIATED $CaMoO_4$

Washing	γ Activity of Tc-99m cpm/ml.	β Activity of impurities cpm/ml.	β Activity after resin treatment cpm/ml.
H_2O	129000	6240	691
1% NH_4OH	74565	12250	—

(2) Twenty milligrams of uranyl nitrate is irradiated in J. R. R.-1 for 2 hr. Neptunium-239 is separated by nitrate form anion exchanger[5]. Then the solution containing uranium and fission products is neutralized with ammonium hydroxide and ammonium biuranate formed is removed by filtering. A few milligrams of ammonium molybdate and lead nitrate are added to this solution. Lead moybdate is separated and washed with water. This precipitate shows a γ-ray spectrum of technetium-99m free from other fission products. (Fig. 1-1)

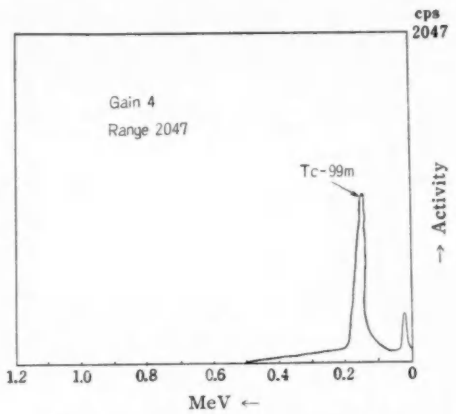


Fig. 1. γ-Ray spectrum of $PbMoO_4$ precipitation.

2. Isolation of Technetium from Fission Products by Anion Exchanger. — Several methods[1,2,6,7] were reported on the separation of technetium-99m from irradiated uranium. These were mainly based on the coprecipitation with sulfide or the solvent extraction. Hall and Johns[8] reported an anion-exchange separation of molybdenum and technetium. According to their results, molybdenum is eluted from a perchlorate form anion exchanger with 10% sodium hydroxide solution, and the technetium is then washed out with 2.0 M ammonium thiocyanate solution. This is a good separation method but thiocyanate solution is unfavorable for further treatment. In another report[9], the dependence of distribution coefficient of technetium on the nitric acid and hydrochloric acid concentrations was measured, and it is known that technetium forms a chloride complex anion within the 0.1~12 N hydrochloric acid concentration range and that it is strongly absorbed at lower nitric acid concentrations, but eluted easily with nitric acid of higher acidity. In the

4) J. A. Swartout, Nat. Nucl. Energy Series, "The Fission Products", Book 2, McGraw-Hill Book Co., Inc., London (1951), Paper 97.
5) F. Ichikawa, This Bulletin, **31**, 778 (1958).
6) D. C. Lincoln and W. H. Sullivan, Nat. Nucl. Energy Series, "The Fission Products", Book 2, McGraw-Hill Book Co., Inc., London (1951), Paper 99.
7) R. P. Schuman, ibid., Paper 100.
8) N. F. Hall and D. H. Johns, *J. Am. Chem. Soc.*, **75**, 5787 (1953).
9) E. H. Huffman, R. L. Oswalt and L. A. Williams, *J. Inorg. Nucl. Chem.*, **3**, 49 (1956).

present paper, the separation of technetium from irradiated uranium by anion exchangers is studied, following the papers mentioned above.

Experimental.—Fifty milligrams of ammonium molybdate is irradiated as mentioned in section 1. The sample is dissolved into 1 or 2 ml. of water and poured on the top of hydroxide form anion exchanger Dowex 1 column (100~200 mesh, 1 cm.×5 cm.). The column is washed with 100 ml. of 10% sodium hydroxide and then technetium is eluted with nitric, hydrochloric or sulfuric acid of various concentrations. Results are shown in Fig. 2-1. From these data, it is shown that technetium is not eluted with 10% sodium hydroxide or 0.7 N nitric acid, but easily eluted with 7 N nitric acid. Then these behaviors are applied to the following experiment.

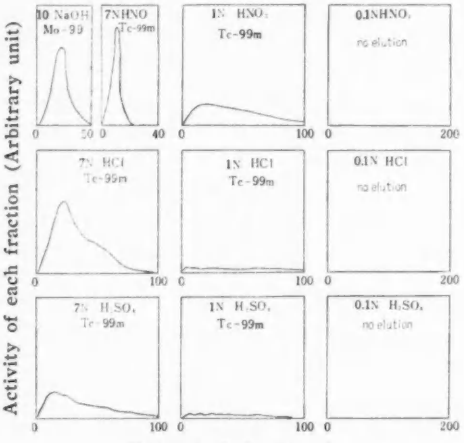


Fig. 2-1. Elution curves of Tc-99m with HNO_3, HCl and H_2SO_4 after elution of Mo-99.

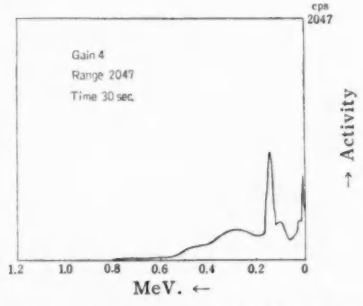


Fig. 2-2. γ-Ray spectrum of total fission products after removal of Np-239.

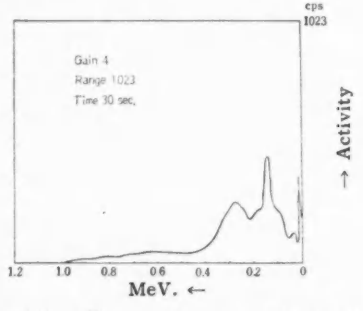


Fig. 2-3. γ-Ray spectrum of 10% NaOH fraction.

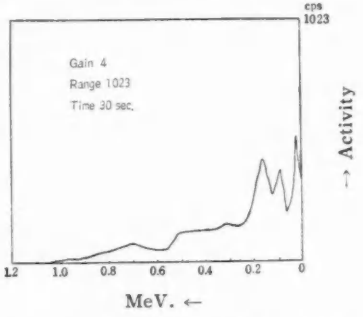


Fig. 2-4. γ-Ray spectrum of 0.7 N HNO_3

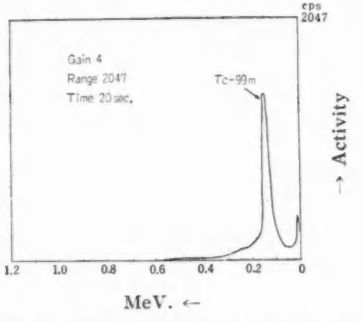


Fig. 2-5. γ-Ray spectrum of 7.5 N HNO_3 fraction.

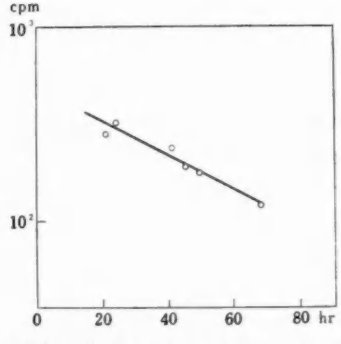


Fig. 2-6. β-Ray decay curve of 7.5 N HNO_3 fraction.

TABLE II. RECOVERY OF TECHNETIUM-99m FROM FISSION PRODUCTS

Exp. No.	Fraction	Total volume of fraction	Sample volume for γ spectrometry	Range of γ spectrometer	Time for measurement	Peak height of Tc-99m	Recovery ratio of Tc-99m
		ml.	ml.	cps	sec.		%
1*	Σ F. p.	50	2	1000	—	27.8	100
	7 N HNO_3	20	2	300	—	62.5	27
				Counts per channel			
2	Σ F. P.	50	2	2047	30	32.3	100
	10% NaOH	70	5	1023	30	26.1	**
	0.7 N HNO_3	50	5	1023	30	0	0
	7 N HNO_3	20	5	2047	20	59.8	46.3

* Data of Expt. No. 1 are measured by single channel pulse height analyzer.
** Tc-99m found in NaOH fraction may be a decay product of Mo-99.

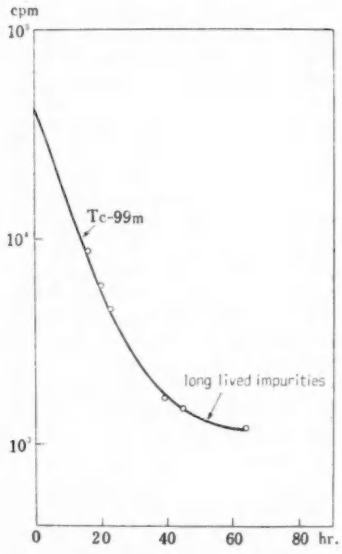


Fig. 2-7. γ-Ray decay curve of 7.5 N HNO_3 fraction.

Twenty milligrams of irradiated uranyl nitrate is used as a starting material. Neptunium-239 is removed by a nitrate form anion exchanger[5]. Thus, about 50 ml. of 7.5 N nitric acid solution of fission products is obtained. This solution is dried up and redissolved in 1 ml. of water and poured onto the hydroxide form anion exchanger. The column is washed with 150 ml. of 10% sodium hydroxide, with 200 ml. of 0.7 N nitric acid and finally with 20 ml. of 7.5 N nitric acid. γ-ray spectra of each fraction are measured by a 256 channel pulse height analyzer. They are shown in Figs. 2-2~5. As Fig. 2-5 shows, the pure spectrum of technetium-99m is found in 7.5 N nitric acid fraction. Decay of β and γ activities are shown in Figs. 2-6 and -7. After 3 days technetium 99m is disintegrated away almost completely, leaving impurities of long half-life.

Results.—Technetium is not eluted with 10% sodium hydroxide and eluted with 3~7 N nitric acid. But with other kinds of acid or dilute nitric acid, the elution of technetium is very slow or unpredictable. This is probably due to the complex formation. Some species of fission products may behave as an anion, and some others may form insoluble hydroxides in these chemical circumstances. These will be caught on a hydroxide form anion exchanger. Species which may form insoluble hydroxide will be eluted with 0.7 N nitric acid. Molybdenum-99 is washed out with sodium hydroxide and other anionic species will be removed with sodium hydroxide and 0.7 N nitric acid.

Recovery of technetium is calculated and shown in Table II. About 40~45% of technetium-99m is recovered in 7.5 N nitric acid solution. Purity in γ-ray activity is about 95% at the separation time.

Thanks are due to Dr. T. Ishimori for his advice and also to Miss S. Uruno, for her able assistance.

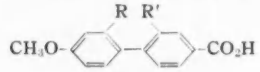
Chemistry Division
Japan Atomic Energy
Research Institute
Tokai, Ibaraki

Estrogenic Biphenyls. V[1]*. Steric Effect in 2,2'-Dialkyl-4-methoxybiphenyl-4'-carboxylic Acids*

By Takeo SATO

(Received February 17, 1959)

Enhancement in the estrogenic activity of the 2- or 2'-alkyl homologs of 4-methoxybiphenyl-4'-carboxylic acid (I) in comparison with the parent compound I was attributed to the increase in the interplanar angle of the two benzene nuclei to attain a favorable conformation[2] for the development of the activity[3].



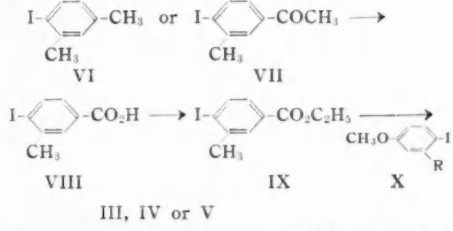
I: R=R'=H
II: R=CH_3, R'=H
III: R=H, R'=CH_3
IV: R=R'=CH_3
V: R=C_2H_5, R'=CH_3

The present author and Ōki also pointed out in the part III[4] of this series that the increase in the chain-length of the alkyl group at position 2 has little effect, as was deduced from the ultraviolet absorption spectra, and, consequently, essentially the same estrogenic potency was found in those compounds.

Since the minimum active dose in mice of the most potent compound of this series was found to be 100 γ, compared with 2.5 γ of stilbestrol dimethyl ether, it is considered that the methylene group at position 2 affords a steric effect which is not optimum for the development of the estrogenic potency as far as the biphenyl derivatives are concerned. Then the author sought higher estrogenic activity in more sterically hindered biphenyl derivatives.

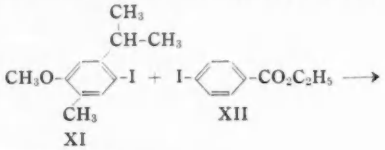
4-Methoxy-2'-methylbiphenyl-4'-carboxylic acid (III) should have a similar conformation with 4-methoxy-2-methylbiphenyl-4'-carboxylic acid (II)[4], as was proved in 2,3'-diethyl-4-methoxybiphenyl-4'-carboxylic acid and 2',5'-diethyl-4-methoxybiphenyl-4'-carboxylic acid[5], because the steric interference by the methyl group must be equivalent at positions 2 and 2'. It is expected that the introduction of another alkyl group into position 2 of the compound III will give more steric interference and will result in a greater rotation of the benzene rings toward each other to relieve the steric hindrance. Thus the thicker models will be given.

The method of preparation is illustrated in the following chart. Although 4-iodo-3-methylbenzoic acid (VIII) was obtained by Klingel[6] through a sequence of reactions starting from *o*-toluidine, the present author largely modified the method as is described in *Experimental Part*. The compound VIII is also obtainable through nitric acid oxidation[7] of 4-iodo-*m*-xylene (VI). The Ullmann reaction between appropriate 4-iodoanisoles (X) and ethyl 4-iodo-3-methylbenzoate (IX) followed by alkaline hydrolysis gave the desired biphenyls.

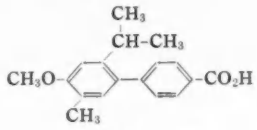


III, IV or V

As a reference compound 2-isopropyl-4-methoxy-5-methylbiphenyl-4'-carboxylic acid (XIII) was prepared from ethyl 4-iodobenzoate (XII) and 4-iodo-3-isopropyl-6-methylanisole (XI). The compound XIII is expected to involve greater rotation of the benzene nuclei toward each other than the corresponding straight-side-chain compounds because of the greater steric interference of the isopropyl group.



1) Part IV: T. Sato and M. Ōki, This Bulletin, **30**, 958 (1957).
2) M. Ōki and Y. Urushibara, ibid., **25**, 109 (1952): See also J. Grundy, *Chem. Revs.*, **57**, 281 (1957).
3) M. Ōki and T. Sato, This Bulletin, **30**, 508 (1957).
4) T. Sato and M. Ōki, ibid., **30**, 859 (1957).
5) M. Ōki and T. Sato, ibid., **30**, 702 (1957).
6) J. Klingel, *Ber.*, **18**, 2687 (1885).
7) A. Grahl, ibid., **28**, 84 (1895).



XIII

The ultraviolet absorption maxima with the estrogenic activities in mice of the compounds I, II, III, IV, V and XIII are given in Table I.

TABLE I. ULTRAVIOLET ABSORPTION MAXIMA AND ESTROGENIC ACTIVITIES OF 4-METHOXY-BIPHENYL-4'-CARBOXYLIC ACID DERIVATIVES

Compound	K-Band maxima λ, mμ	log ε	Active dose in mice, γ (%)
I	289	4.36	1000 (50)
II	280	4.17	200 (100)
III	271	4.21	
IV			100 (80)
V			100 (60)
XIII	273	4.06	

The ultraviolet absorption maximum of the compound III is located at 271 mμ and the curve is similar with that of compound II. The hypsochromic shift in the type of the compound III compared with the compound II is always observed and may be attributed to the hyperconjugation of the methyl group[8]. The compound XIII, even though the bulkiness of the isopropyl group is expected to exert a greater steric interference and to cause a greater deterioration in conjugation, still possesses a strong K-band of the biphenyl system. The hypsochromic shift of the absorption maximum of the compound XIII, which can be compared with the compound II in term of hyperconjugation, can be attributed to the deterioration in conjugation, since the methyl group at position 5 is known to have little effect on the ultraviolet absorption[9]. On the other hand, the compounds IV and V show weak absorption at about 280 mμ, possess instead the strong absorption at about 230 mμ, indicating the two moieties of the biphenyl system absorb the light almost independently. Thus the two benzene nuclei in the compounds IV and V are considered nearly perpendicular to each other.

The estrogenic activity in ovariectomized mice was determined by the vaginal smear test. It is striking to find out that the estrogenic potency is not greatly altered by the introduction of the alkyl groups into position 2 and/or posititon 2', but it is evident that the estrogenic action is enhanced by the introduction of the alkyl groups.

Experimental[10]

4-Amino-3-methylacetophenone. — To a well stirred mixture of 115 g. (0.77 mol.) of *o*-acetotoluidide, 70 g. (0.89 mol.) of acetyl chloride and 700 ml. of carbon disulfide, was added 350 g. (2.62 mol.) of anhydrous aluminum chloride in small portions in the course of one hour, during which time the whole was gently refluxed on a bath. The refluxing was continued for one hour and the viscous oil at the bottom, after cooling, was decomposed with an excess of concentrated hydrochloric acid. The acidic mixture was hydrolyzed by refluxing for two hours without isolation of the acetamido compound. The solution was made alkaline with sodium hydroxide and the organic material was extracted with ether. The ethereal solution was washed as usual and evaporated to give 44 g. (38% of the theoretical) of 4-amino-3-methylacetophenone, colorless needles, which melted at 110°C on recrystallization from benzene-petroleum ether. The reported melting point is 102°C[5].

Anal. Found: N, 9.52. Calcd. for $C_9H_{11}NO$: N, 9.39%.

4-Iodo-3-methylacetophenone (VII).—To a diazonium solution obtained from 16 g. (0.11 mol.) of 4-amino-3-methylacetophenone, 30 ml. of concentrated sulfuric acid, 100 ml. of water and 7 g. (0.10 mol.) of sodium nitrite in minimum quantity of water, was added a solution of 17 g. (0.1 mol.) of potassium iodide in 20 ml. of water in the course of 10 min. Stirring was continued for thirty minutes below 10°C and then at 50°C for one hour. The mixture was extracted with ether and the ethereal extract was successively washed with aqueous sodium hydroxide, aqueous sodium thiosulfate and water. The iodo-acetophenone boiled at 146~148°C/8 mm. and solidified on standing. Pale yellow crystals, m. p. 42~43°C. Yield, 15.5 g. or 60% of the theoretical. It was prepared by Klingel[6] in the same way and the reported melting point was 39°C.

4-Iodo-3-methylbenzoic acid (VIII).—A solution of 45 g. (0.17 mol.) of iodoketone VII in 170 ml. of dioxane was dropped slowly into a sodium hypobromite solution, made from 56 g. (1.4 mol.) of sodium hydroxide, 82 g. (0.51 mol.) of bromine and 450 ml. of water, at the temperature below 10°C. After the excess of sodium hypobromite was decomposed with sodium bisulfite and bromoform was removed by steam distillation, the solution was acidified to give a crystalline substance, which was recrystallized from ethanol-water. Colorless needles, m. p. 198~199°C. Yield, 39 g. (88% of the theoretical). According to

8) Private communication from Dr. M. Ōki, the University of Tokyo.
9) T. Sato and M. Fujii, unpublished work.
10) All melting and boiling points are uncorrected. The microanalyses were carried out by Mr. Mizushima to whom the author's thanks are due.

Klingel[6] the same acid, m. p. 203~204°C, was obtained by chromic acid oxidation of the iodoketone VII.

Anal. Found: C, 36.72; H, 2.72. Calcd. for $C_9H_7O_2I$: C, 36.66; H, 2.69%.

Ethyl 4-iodo-3-methylbenzoate (IX).—The iodobenzoate was obtained as a colorless oil boiling at 145~147°C/8 mm. by usual esterification of the acid VIII.

Anal. Found: C, 41.21; H, 3.79. Calcd. for $C_{10}H_{11}O_2I$: C, 41.41; H, 3.82%.

4-Methoxy-2'-methylbiphenyl-4'-carboxylic acid (III).—As a general procedure of the Ullmann reaction, the preparation of 4-methoxy-2'-methylbiphenyl-4'-carboxylic acid (III) is described. To a well-stirred mixture of 3 g. (0.010 mol.) of ethyl 3-methyl-4-iodobenzoate (IX) and 10 g. (0.043 mol.) of 4-iodoanisole (X, R=H), 10 g. (0.16 atom) of copper bronze, activated by Kleiderer and Adams' method[11], was added in 20 min. at 220~230°C. The reaction mixture was then heated to 270~280°C for 25 min. and extracted with acetone after cooling. The extract was hydrolyzed by refluxing with a mixture consisting of 50 ml. of 10% sodium hydroxide solution and 100 ml. of ethanol for about two hours. The solvent was evaporated and the residue was diluted with water. Insoluble dimethoxybiphenyl was removed by filtration. On acidification, the filtrate afforded an acid mixture, which was purified by chromatography on alumina. Repeated recrystallizations from ethanol gave 500 mg of colorless needles, m. p. 183~184°C.

Anal. Found: C, 73.92; H, 5.59. Calcd. for $C_{15}H_{14}O_3$: C, 74.36; H, 5.83%.

2, 2'-Dimethyl-4-methoxybiphenyl-4'-carboxylic acid (IV).—The dimethylbiphenyl was prepared from compound IX and 4-iodo-3-methylanisole (X, R=CH_3)[4]. It was necessary to remove unchanged starting materials in vacuo before hydrolysis for the easier purification of the product. The acid was obtained as colorless prisms on recrystallization from ethanol-water, m. p. 142~144°C.

Anal. Found: C, 74.99; H, 6.39. Calcd. for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29%.

2-Ethyl-4-methoxy-2'-methylbiphenyl-4'-carboxylic acid (V).—It was prepared from IX and 3-ethyl-4-iodoanisole (X, R=C_2H_5)[3]. Removal of the unchanged materials in vacuo was required and the distillate up to 180°C/5 mm. was discarded. Colorless needles, m. p. 139~140°C were obtained on recrystallization from benzene-petroleum ether.

Anal. Found: C, 75.55; H, 6.75. Calcd. for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71%.

2-Isopropyl-5-methyl-4-iodoanisole (XI). — To a solution of 80 g. (0.49 mol.) of carvacrol methyl ether in 100 ml. of ethanol were alternatively added 130 g. (0.51 mol.) of iodine and 130 g. (0.60 mol.) of yellow mercuric oxide in small portions in the course of 30 min., while the mixture was well stirred and cooled in ice-water below 20°C. Stirring was continued for an additional 30 min. The mixture was heated on a water bath for 10 min. and filtered with suction. After the filtrate was diluted with water, the heavy oil was extracted with ether. The ethereal solution was washed with aqueous potassium iodide and dried over calcium chloride. The product boiling at 130~150°C/6~7 mm. was collected and then refractionated. The pure compound was obtained as brown oil, b. p. 135~137°C/6 mm.

Anal. Found: C, 46.16; H, 5.21. Calcd. for $C_{11}H_{15}OI$: C, 45.53; H, 5.21%.

2-Isopropyl-4-methoxy-5-methylbiphenyl-4'-carboxylic acid (XIII). — It was prepared from the compound XI and ethyl 4-iodobenzoate (XII). After hydrolysis the acidic portion was extracted with ethanol and the extract was recrystallized from ethanol to give colorless plates, m. p. 227.5~229°C.

Anal. Found: C, 76.06; H, 6.98. Calcd. for $C_{18}H_{20}O_3$: C, 76.03; H, 7.09%.

Ultraviolet absorption spectra. — They were measured with a Hitachi photoelectric spectrophotometer Model EPU-2, the compounds being in dissolved 95% ethanol.

The author wishes to express his hearty thanks to Professor Y. Urushibara, the University of Tokyo, Professor K. Hata, Tokyo Metropolitan University, and Dr. M. Ōki for their kind guidance and encouragement throughout this study and to the members of the Research Department, Teikoku Hormone Manufacturing Co., Ltd., Kawasaki, for bioassays. The author is also indebted to the Ministry of Education for the Grant in Aid for Fundamental Scientific Research.

Department of Chemistry
Faculty of Science
Tokyo Metropolitan University
Setagaya-ku, Tokyo

11) E. C. Kleiderer and R. Adams, *J. Am. Chem. Soc.*, 55, 4219 (1933).

The Aconite Alkaloids. XXXII[1]. *On Lucidusculine. Part II*[2]

By Takashi AMIYA

(Received March 2, 1959)

In the previous report[2] the extended formula of lucidusculine (I) has been proposed as follows:

$$C_{18}H_{23}\begin{cases}(OH)_2\\OCOCH_3\\>N-C_2H_5\\>C=CH_2\end{cases}$$

Some new derivatives of lucidusculine are described in the present paper.

Catalytic hydrogenation[3] of I with platinum oxide in glacial acetic acid yielded dihydrolucidusculine(II), $C_{24}H_{37}O_4N$, m. p. 192~198°C, $[\alpha]_D^{18}$ −58.6°. On acetylation with acetic anhydride in pyridine, II gave dihydrolucidusculine diacetate(III), $C_{28}H_{41}O_6N$, m. p. 140~144°C, $[\alpha]_D^{18}$ −55.5°.

The infrared absorption spectrum of compound I gave two peaks at 6.06 and 11.26 μ and that of lucidusculine diacetate (IV)[4,5], $C_{28}H_{39}O_6N$, gave peaks at 6.08 and 11.32 μ due to presence of a terminal methylene group. Compounds II and III, on the other hand, showed no peak near the above-mentioned wavelengths. Therefore, it seems very probable that the hydrogenation of compound I proceeds as:

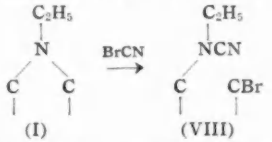
$$>C=CH_2 \xrightarrow{2H} >\overset{*}{C}H-CH_3$$

On account of a newly formed asymmetric carbon atom (asterisked) the formation of an epimer of compound II might be suspected[6].

Luciculine(V), $C_{22}H_{33}O_3N\cdot H_2O$, obtained from compound I upon hydrolysis with alcoholic potassium hydroxide[5], also showed two peaks in the infrared spectrum at 6.09 and 11.27 μ characteristic of a terminal methylene group.

Hofmann degradation of luciculine methiodide(VI) yielded a basic substance, named isomesoluciculine[7](VII), $C_{21}H_{31}O_2N\cdot H_2O$, m. p. 123~127°C (decomp.), $[\alpha]_D^{19}$ −17.0°. Compound VII showed peaks in the infrared spectrum at 6.08 and 11.28 μ characteristic of a terminal methylene group.

On treatment of compound I with cyanogen bromide, two reaction products were obtained. One of them was easily isolated because of its high solubility in water; it was named bromolucidusculine cyanamide (VIII), $C_{24}H_{35}O_4N(CN)Br\cdot 2H_2O$, m. p. 157~162°C (decomp.), $[\alpha]_D^{17}$ −76.0°, in which cleavage of the N-containing ring was noticed. It showed a peak in the infrared spectrum at 4.74 μ due to presence of a cyano group. The other was easily soluble in acetone but found to crystallize with difficulty. This cyanogen bromide degradation may proceed as follows:



The ultraviolet absorption spectra of all these compounds showed only end absorptions and are reminiscent of those of aconite alkaloids, i.e., atisine, dihydroatisine, aconine, delphonine[8] and lycoctonine[9].

Experimental

Lucidusculine (I).—The ultraviolet absorption spectrum of this compound in methanol showed end absorption and no maximum. The infrared absorption spectrum in Nujol showed the presence of hydroxyl groups (2.95 μ), an acetoxyl group (5.82 and 8.10 μ) and a terminal methylene group (6.06 and 11.26 μ).

Dihydrolucidusculine (II).—Lucidusculine (1 g.)

1) This constitutes a part of a series entitled "The Aconite Alkaloids" by H. Suginome. Part XXXI: T. Shima and T. Amiya, This Bulletin, **31**, 657 (1958).

2) Part I: H. Suginome, T. Amiya and T. Shima, ibid., **32**, 824 (1959).

3) Cf. H. Suginome and F. Shimanouchi, *Ann.*, **545**, 220 (1940), Foot Note 4).

4) H. Suginome, S. Kakimoto and J. Sonoda, *J. Fac. Sci., Hokkaido Univ., Ser. III. Chem.*, **4**, 25 (1950).

5) R. Majima and S. Morio, *Ber.*, **65**, 599 (1932).

6) This point will be mentioned later.

7) By the same treatment, H. Suginome and S. Umezawa obtained mesoluciculine, $C_{21}H_{31}O_3N\cdot H_2O$, m.p. 199~200°C with sintering point 114°C, $[\alpha]_D^{15}$ −12.8°, H. Suginome and S. Umezawa, *J. Fac. Sci., Hokkaido Univ., Ser. III. Chem.*, **4**, 44 (1950). The relation between mesoluciculine and isomesoluciculine seems to be that of polymorphism.

8) L. C. Craig, L. Michaelis, S. Granick and W. A. Jacobs, *J. Biol. Chem.*, **154**, 293 (1944).

9) O. E. Edwards and Léo Marion, *Canad. J. Chem.*, **30**, 627 (1952).

was dissolved in 16 cc. of glacial acetic acid and hydrogenated with 0.5 g. of platinum oxide for six hours. After removal of platinum, the solution was evaporated to dryness. On treatment of the residue with water and then with aqueous ammonia, a precipitate was obtained. On recrystallization from ethyl acetate, crystals were yielded, which melted at 192~198°C. $[\alpha]_D^{18}$ −58.6° (methanol). Yield, 0.5 g. The ultraviolet absorption spectrum of this compound in methanol showed end absorption and no maximum. The infrared absorption spectrum in Nujol showed the presence of hydroxyl groups (2.96 μ) and an acetoxyl group (5.80 and 8.12 μ).

Anal. Found: C, 70.61; H, 9.15. Calcd. for $C_{24}H_{37}O_4N$: C, 71.43; H, 9.24%.

Dihydroluciduscuiline Diacetate (III). — A mixture of dihydroluciduscuiline (0.6 g.), acetic anhydride (1 cc.) and pyridine (4 cc.) was allowed to stand in a sealed tube at room temperature for two days. After removal of the solvents, the residue was dissolved in water and then precipitated with aqueous ammonia. The precipitate was recrystallized from ethanol. Crystals melted at 140~144°C. $[\alpha]_D^{18}$ −55.5° (methanol). Yield was quantitative. The ultraviolet absorption spectrum of this compound in methanol showed end absorption and no maximum. The infrared absorption spectrum in Nujol had no peak attributable to a hydroxyl group but showed the presence of acetoxyl groups (5.82 and 7.95 μ).

Anal. Found: C, 68.45; H, 8.84. Calcd. for $C_{28}H_{41}O_6N$: C, 68.96; H, 8.48%.

Luciduscuiline Diacetate (IV). — A mixture of luciduscuiline (0.6 g.), acetic anhydride (1 cc.) and pyridine (4 cc.) was allowed to stand in a sealed tube at room temperature for two days. After removal of the solvents, the residue was dissolved in water and then precipitated with aqueous ammonia. The precipitate was recrystallized from ethanol. Crystals melted at 159~167°C alone and on admixture with luciduscuiline diacetate prepared according to the direction of Majima and Morio[4,5]. Yield was quantitative. The ultraviolet absorption spectrum of this compound in methanol showed end absorption and no maximum. The infrared absorption spectrum in Nujol showed the presence of acetoxyl groups (5.82 and 8.01 μ) and a terminal methylene group (6.08 and 11.32 μ).

Luciculine (V). — The ultraviolet absorption spectrum of this compound in methanol showed end absorption and no maximum. The infrared absorption spectrum in Nujol showed the presence of hydroxyl groups (2.98 μ) and a terminal methylene group (6.09 and 11.27 μ).

Luciculine Methiodide (VI).—The ultraviolet absorption spectrum of this compound in methanol showed end absorption and no maximum. The infrared absorption spectrum in Nujol had a peak at 2.98 μ attributable to hydroxyl groups and peaks at 6.11 and 11.22 μ attributable to a terminal methylene group.

Isomesoluciculine (VII). — The base was prepared from luciculine methiodide (0.5 g.) by Hofmann degradation. Recrystallization from acetone gave crystals, which melted at 123~127°C (decomp.). $[\alpha]_D^{19}$ −17.0° (methanol). The ultraviolet absorption spectrum of this compound in methanol showed end absorption and no maximum. The infrared spectrum in Nujol showed the presence of hydroxyl groups (2.98 μ) and a terminal methylene group (6.08 and 11.28 μ).

Anal. Found: C, 68.79; H, 9.31; (N)CH_3, 4.52; H_2O, 5.04. Calcd. for $C_{21}H_{31}O_3N \cdot H_2O$: C, 69.39; H, 9.15; (N)$CH_3$, 4.13; H_2O, 4.95%.

Bromoluciduscuiline Cyanamide (VIII). — To cyanogen bromide (0.25 g.) dissolved in 7.5 cc. of benzene, luciduscuiline (0.45 g.) dissolved in benzene (16 cc.) was added. The reaction mixture, which became turbid after 10 min., was allowed to stand at room temperature for 24 hr. and then was filtered. The crystalline precipitate collected by filtration was hygroscopic and then treated with water. The residue, obtained from the water-soluble portion, was crystallized from acetone and melted at 157~162°C (decomp.). $[\alpha]_D^{17}$ −76.0° (methanol). The ultraviolet absorption spectrum of this compound in methanol showed end absorption and no maximum. The infrared absorption spectrum in Nujol showed the presence of hydroxyl groups (2.94 and 3.10 μ), a cyano group (4.74 μ), an acetoxyl group (5.88 and 7.97 μ) and a terminal methylene group (6.06 and 11.23 μ).

Anal. Found: C, 55.92; H, 7.89; N, 4.52; Br, 13.66; (N)C_2H_5, 4.94; H_2O, 5.5. Calcd. for $C_{24}H_{33}O_4N(CN)Br \cdot 2H_2O$; C, 55.23; H, 7.23; N, 5.13; Br, 14.70; (N)C_2H_5, 5.34; H_2O, 6.62%.

The water-insoluble portion did not crystallize from acetone. These portions were nearly equal in amounts.

The author wishes to express his sincere thanks to Professor Harusada Suginome, President of Hokkaido University, for his kind guidance throughout this work and to Mr. Mineo Yakushiji for the determination of *N*-alkyl groups.

Department of Chemistry
Faculty of Science
Hokkaido University
Sapporo

Intramolecular Interaction between Hydroxyl Group and π-Electrons. VI[1]*. Electronic Effect on the Interaction in ω-Arylalkanols*

By Michinori Ōki and Hiizu Iwamura

(Received March 17, 1959)

In connection with the intramolecular interaction between hydroxyl group and π-electrons, the authors have measured the ν_{O-H} absorption of various substituted benzyl alcohols and concluded that the hydrogen atom of the hydroxyl group interacts with the π-electron on the carbon atom to which the hydroxymethyl group is attached. On the other hand, Goldman and Crisler[2] examined three phenethyl alcohol derivatives on the O–H stretching absorption and concluded that the hydrogen atom of the hydroxyl group interacts with the π-electron on the carbon atom to which the 2-hydroxyethyl group is attached. Meanwhile, the present authors predicted[3], by comparison of the two band intensities of the interacting forms in allyl alcohol and 3-buten-1-ol, that the interaction occurring in them might be different in nature, since allyl alcohol gives a larger band intensity of the interacting form than 3-buten-1-ol in spite of the fact that $\Delta\nu_{max}$ is smaller in allyl alcohol than in 3-buten-1-ol. Moreover, it is reasonable to consider that allyl alcohol with benzyl alcohol and 3-buten-1-ol with phenethyl alcohol possess the same type of interaction. Therefore, it may be thought that there is a contradiction between the conclusion by Goldman and Crisler and that by the present authors. Since it is dangerous to draw a conclusion from a small number of examples, the ν_{O-H} absorptions of various ω-arylalkanols have been re-examined.

Experimental

Measurement.—It was performed similarly as described previously[3]. When a small peak was present (3-arylpropanols) or the presence of a peak was suspected (4-arylbutanol), the measurement was carried out with a quartz cell of 5 cm. length without alteration of concentration.

Calculation of Integrated Intensities.—It was carried out similarly as reported previously[3], when only two bands were present. However, the presence of three bands, two of which were derived from the presence of the rotational isomers and the third by the internal interaction, required modification to some extent. The two stronger bands were first obtained in the usual manner and the summation of the bands was subtracted from the apparent curve. This procedure usually gave rise to an unsymmetric band. The process was repeated through the trial-and-error method until the third band became symmetric.

Materials.—The compounds used for the measurement are known compounds, unless otherwise stated, and their physical constants well agree with those in the literature.

Preparation of ω-Arylalkanols by Lithium Aluminum Hydride Reduction of Esters.—To a slurry prepared from 2.5 g. (0.07 mol.) of lithium aluminum hydride and 100 ml. of ether, was added 0.1 mol. (0.05 mol. for amino-esters) of the corresponding ester[4]. After stirring for two hours at the room temperature, the excessive lithium aluminum hydride was decomposed by adding ethyl acetate in ether and then dilute sulfuric acid (aqueous sodium hydroxide in the case of aminoalcohols) was added. The aqueous layer was extracted with ether and ethereal extract was washed with aqueous sodium hydroxide. After drying over potassium carbonate followed by evaporation, the residue was either fractionally distilled or recrystallized from an appropriate solvent. Compounds with low melting points were once distilled and then recrystallized. The results are summarized in Table I.

Preparation of 2-(*m*-Aminophenyl)-ethanol.—2-(*m*-Aminophenyl)-ethanol (V) was prepared as illustrated in the following chart.

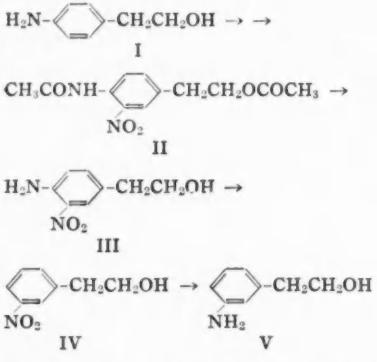
1) Part V of this series: This Bulletin, **32**, 955 (1959).
2) I. M. Goldman and R. O. Crisler, *J. Org. Chem.*, **23**, 751 (1958).
3) M. Ōki and H. Iwamura, This Bulletin, **32**, 567 (1959).

4) Amino-esters were conveniently prepared by hydrogenation of the corresponding nitro-esters or alkyl nitrocinnamates in the presence of U-Ni-A catalyst [Y. Urushibara, S. Nishimura and H. Uehara, This Bulletin, **28**, 466 (1955)]. Substituted cinnamic acids were also reduced with the same catalyst in excellent yields, when their sodium salts in water were used. The authors are grateful to Dr. S. Nishimura for hydrogenation.
5) See; N. Carmack and M. A. Spielman, "*Organic Reactions*", John Wiley & Sons, Inc., New York, Vol. III, (1946), p. 83; E. Schwenk and E. Bloch, *J. Am. Chem. Soc.*, **64**, 3051 (1942).
6) C. J. Collins, ibid., **73**, 1038 (1951).
7) D. Sontag, *Compt. rend.*, **197**, 159 (1933).

TABLE I. ω-ARYLALKANOLS [x-$RC_6H_4(CH_2)_nOH$]

R	x	n	b. p. (°C) (3 mmHg)	m. p. (°C)	Crystal form	n_D		*Anal.* Calcd.	Found
Cl[a]	*m*	2	100.5	—	—	1.5475 (23°C)	C:	61.35	61.59
							H:	5.73	6.00
CH_3[b]	*p*	3	97～98	23～25	plates	—	C:	79.95	79.68
							H:	9.39	9.28
H_2N[c]	*p*	3	145～150	54～55	needles	—	C:	71.49	71.26
							H:	8.67	8.70
Cl[d]	*p*	3	111～112	—	—	1.5428 (15.5°C)	C:	63.35	63.87
							H:	6.49	6.59
H_2N[e]	*p*	4	—	71～72	needles	—	C:	72.69	72.50
							H:	9.15	9.24

a) The starting material, methyl *m*-chlorophenylacetate, was conveniently prepared through the modified Wilgerodt reaction[5] using morpholine and *m*-chloroacetophenone followed by hydrolysis and then esterification. The over-all yield of the ester was 70%.
b) The melting point has not been reported[6].
c) Recrystallized from benzene containing a small amount of alcohol.
d) Refractive index was reported as 1.5424 (21°C) for substance obtained by the chlorination of 3-phenylpropanol[7].
e) This compound is rather unstable and discolors quickly in the air. Benzene was used as the recrystallization solvent.



2-(p-Acetamido-m-nitrophenyl)-ethyl acetate (*II*). To 102 g. (1 mol.) of acetic anhydride, 118 g. (0.86 mol.) of 2-(*p*-aminophenyl)-ethanol[8] was added and the mixture was heated on a water bath for thirty minutes. After cooling, 79 g. (1 mol.) of acetyl chloride was slowly added, and the mixture was heated under reflux on a water bath for one hour. Hydrogen chloride and the excessive reagents were removed in vacuo and the residue was dissolved in 400 ml. of acetic anhydride. The solution was cooled in an ice-salt bath and 106.5 ml. (1.7 mol.) of nitric acid (d=1.42) was carefully added at 10～20°C with good stirring. The mixture was stirred for further fifteen minutes at that temperature and then poured into 3 l. of ice-water. The crystals were collected and the major portion was submitted to the subsequent hydrolysis. The analytical sample was obtained by recrystallization from benzene-petroleum ether. It was obtained as yellow needles, m. p. 77°C.

Anal. Found: C, 53.95; H, 5.48. Calcd. for $C_{12}H_{14}N_2O_5$: C, 54.15; H, 5.25%.

8) H. M. Woodburn and C. F. Stuntz, *J. Am. Chem. Soc.*, **72**, 1362 (1950).

2-(p-Amino-m-nitrophenyl)-ethanol (*III*). — The crude compound II was heated with 500 ml. of 6 N hydrochloric acid under reflux for three hours. The cooled reaction mixture was basified with aqueous sodium hydroxide and organic material was extracted with ether. The ethereal extract was dried over potassium carbonate and evaporated. The residue solidified on standing and was recrystallized from benzene. Orange flat needles, m. p. 85～87°C. Over-all yield, 88 g. (56%).

Anal. Found: C, 52.86; H, 5.63. Calcd. for $C_8H_{10}N_2O_3$: C, 52.74; H, 5.53%.

2-(m-Nitrophenyl)-ethanol (*IV*).—To a solution of 54.6 g. (0.2 mol.) of compound III in 80 ml. of concentrated hydrochloric acid and 20 ml. of water, was added 20.7 g. (0.3 mol.) of sodium nitrite in a minimal quantity of water at −5～−3°C. The mixture was stirred at 0°C for ten minutes and then 325 g. (1.5 mol.) of 30% hypophosphorus acid precooled to 0°C was added, the temperature being maintained at 0～3°C. The mixture was stirred for another hour and then allowed to stand in an ice-bath containing ca. 5 kg. of ice which melted in about twelve hours. After twenty-four hours, the mixture was extracted with ether and the ethereal extract was washed with aqueous sodium hydroxide. Drying with potassium carbonate followed by fractional distillation afforded 25.0 g. (50%) of an orange-yellow oil, b. p. 141～146°C/4 mm., which set to needles. The analytical sample was obtained through recrystallization from benzene-petroleum ether. It was obtained as faintly yellow needles, m. p. 50～51°C.

Anal. Found: C, 57.58; H, 5.55. Calcd. for $C_8H_9NO_3$: C, 57.38; H, 5.43%.

2-(m-Aminophenyl)-ethanol (*V*)[9].—To a solution

9) This compound has been prepared by lithium aluminum hydride reduction of *m*-aminophenylacetic acid [J. B. Dickey and E. B. Towne, Brit. Pat., 722,367; *Chem. Abstr.*, **49**, 9935 (1955)]. They reported only the boiling point as 135～138°C/2 mm. but no melting point.

TABLE II. ν_{O-H} ABSORPTIONS OF 2-ARYLETHANOLS (x-$RC_6H_4CH_2CH_2OH$)

R	x	OH	ν_{max} (cm^{-1})	$\Delta\nu^{\circ}_{1/2}$ (cm^{-1})	$A\times10^{-3}$ ($mol^{-1}\cdot l.\cdot cm^{-2}$)	$\Delta\nu_{III-I}$ (cm^{-1})	$A_I/(A_{II}+A_{III})$
		I	3598.0	25.6	3.62		
	m	II	3625	18	0.60	37.5	1.50
H_2N		III	3635.5	17.6	1.82		
		I	3597.8	24.4	3.14		
	p	II	3623	18	0.53	37.2	1.14
		III	3635.0	19.8	2.23		
		I	3602.3	24.8	3.34		
	m	II	3624	18	0.66	33.5	1.19
CH_3O		III	3635.8	17.9	2.14		
		I	3602.5	26.4	2.96		
	p	II	3623	18	0.69	33.3	1.03
		III	3635.8	18.0	2.19		
		I	3603.1	27.3	3.28		
	m	II	3625	20	0.82	32.7	1.06
CH_3		III	3635.8	18.1	2.27		
		I	3602.1	22.4	2.72		
	p	II	3623	20	0.74	33.2	0.93
		III	3635.5	17.0	2.19		
		I	3606.4	24.4	2.62		
H		II	3626	17	0.68	29.6	0.86
		III	3636.0	18.4	2.36		
		I	3611.0	23.0	2.25		
	m	II	3625	16	0.71	24.2	0.645
Cl		III	3635.2	15.8	2.78		
		I	3610.2	24.4	2.23		
	p	II	3625	17	0.88	25.3	0.64
		III	3635.5	15.2	2.61		
		I	3615.0	21.6	1.20		
	m	II	3625	17	1.52	20.0	0.207
O_2N		III	3635.0	15.4	4.29		
		I	3614.0	22.4	1.37		
	p	II	3626	18	1.42	21.0	0.253
		III	3635.0	14.6	3.99		

of 90 g. (0.36 mol.) of 90% stannous chloride in 80 ml. of concentrated hydrochloric acid, was added 20 g. (0.12 mol.) of compound IV and the mixture was stirred, when the spontaneous reaction set in. After the reaction subsided, the mixture was heated on a water bath for thirty minutes, cooled and decomposed with an excess of aqueous sodium hydroxide. When the mixture was chilled, the aminoalcohol solidified and was collected by filtration. It was recrystallized from benzene, m. p. 68~69°C. It sometimes forms needles and sometimes plates. Yield, 13 g. (80%).

Anal. Found: C, 70.00; H, 7.98. Calcd. for $C_9H_{11}NO$: C, 70.04; H, 8.08%.

Results and Discussion

2-Arylethanols. — The apparent O-H stretching absorption curves are divided into three, assuming that they are the overlap of the three symmetric bands which are expressed by Lorentz function. The apparent curves refuse to be divided into two to fit in, as was pointed out in the earlier paper[3]. The results are shown in Table II.

The actual features of division are shown in Fig. 1 and Fig. 2, 2-(*p*-aminophenyl)-ethanol and 2-(*p*-nitrophenyl)-ethanol being taken as the examples because of the extremity of Hammett's σ-values of the substituents.

Two (bands II and III) of the three ν_{O-H} absorption bands are derived from the rotational isomers of primary alcohols and their positions (3635 cm^{-1} and 3625 cm^{-1}) are in good agreement with the previous assignment[10]. The third band (band I) must be attributed to the presence of the intramolecular interation between the hydroxyl group and the π-electrons as

10) M. Ōki and H. Iwamura, This Bulletin, **32**, 950 (1959).

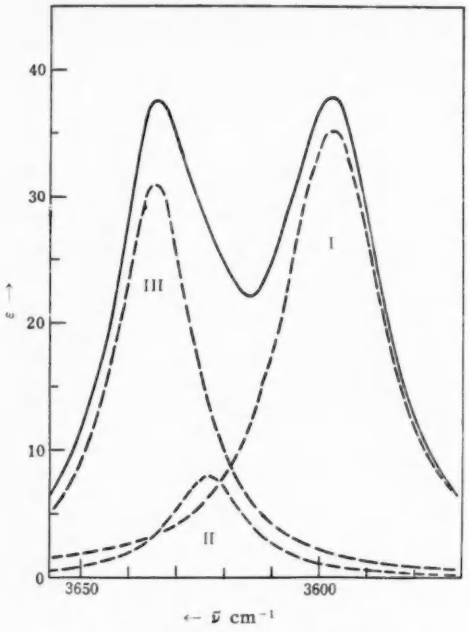


Fig. 1. ν_{O-H} absorption of 2-(*p*-aminophenyl)-ethanol.

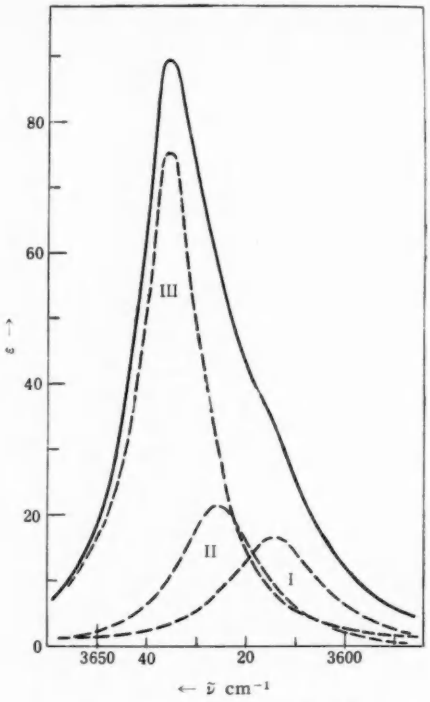


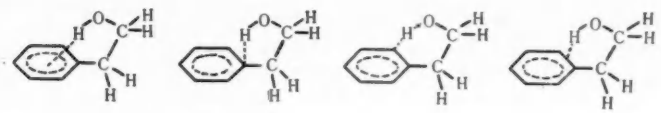
Fig. 2. ν_{O-H} absorption of 2-(*p*-nitrophenyl)-ethanol.

Trifan and his coworkers[11,12], Anet and Bavin[13] and Goldman and Crisler[2] have assigned. Since the error involved in dividing the original band into three is rather great, especially for band II, it is not allowable to use the integrated intensity of band II for discussion, although molecular scale models tell that band II is derived from the only rotational form that makes the interaction possible. Hence, the difference of the wave numbers is shown by $\nu_{III}-\nu_I$ rather than by $\nu_{II}-\nu_I$ and the ratio of the integrated intensities is also exemplified by $A_I/(A_{II}+A_{III})$ rather than by A_I/A_{II}.

As clearly understood from Table II, the electronic effect from the substituent is observed. The wave number of the ν_{O-H} absorption maximum (band I) of the interacting form shifts to a lower wave number as the substituent becomes more electron-releasing, and the electron-attracting substituent causes the wave number of band I to shift and approach to the absorption of normal primary alcohols, this phenomenon having not been observed in benzyl alcohol derivatives. The integrated intensity of band I also increases as the electron-releasing group is introduced.

As to the molecular structure of the internally interacting form, the authors pointed out four possibilities as shown in Fig. 3[1]. Structure VI indicates the interaction between the hydroxyl group and the benzene nucleus as a whole, the case having been suggested by Trifan and his coworkers[11]. Structure VII, representing the interaction which includes C_1 of the benzene nucleus, was deduced by Goldman and Crisler[2] by comparison of three ν_{O-H} curves of 2-phenylethanol, 2-(*p*-methoxyphenyl)-ethanol and 2-(*p*-nitrophenyl)-ethanol. Structure VIII with the participation of C_2 of the benzene nucleus was suggested by Lüttke and Mecke[14], and structure IX, in which C_1 and C_2 take part, by Baker and Shulgin[15].

11) D. S. Trifan, J. L. Weinmann and L. P. Kuhn, *J. Am. Chem. Soc.*, **76**, 6566 (1957).
12) P. von Schleyer, D. S. Trifan and R. Bacskai, ibid., **80**, 6691 (1958).
13) F. A. L. Anet and P. M. G. Bavin, *Can. J. Chem.*, **34**, 1756 (1956).
14) W. Lüttke and R. Mecke, *Z. Elektrochem.*, **53**, 241 (1949); *Z. physik. Chem.*, **196**, 56 (1950).
15) A. W. Baker and A. T. Shulgin, *J. Am. Chem. Soc.*, **80**, 5358 (1958).



VI VII VIII IX

Fig. 3.

Structure VII is first excluded on the basis of the experimental results given in Table II, because compounds with the same substituent in the meta and in the para positions to the 2-hydroxyethyl group give similar curves. Structure VII expects a favored interaction in the 2-phenylethanol with a strongly electron-donating group in the para position over the compound possessing the same substituent in the meta.

Structure VI is rather improbable because it has no orbital which would couple with that of the hydrogen atom. If such interaction took place, further lengthening of the O–H bond should be expected, which would give rise to further lowering of the wave number of band I because of a weaker force constant. Structure VI is made improbable also by the theoretical treatment of the complex of benzene with hydrogen ion or silver ion as discussed below. The structure should not be hexagonally symmetrical, nor should the positive ion be on the plane of the benzene nucleus[16].

Thus, there are two possibilities left for the structure. It seems that structure VIII is more convincing when Hammett's σ values[17] of the ortho position in respect of 2-hydroxyethyl group is taken for the ordinate and $\log \frac{A_I/(A_{II}+A_{III})}{[A_I/(A_{II}+A_{III})]_0}$, where $[A_I/(A_{II}+A_{III})]_0$ is the ratio obtained with 2-phenylethanol, for the abscissa (Fig. 4), because they are nearly in linear relation. However, the defect of this structure can be pointed out immediately because of the far deviation of 2-(*p*-methoxyphenyl)-ethanol from a straight line, or, in other words, because 2-(*p*-methoxyphenyl)-ethanol and 2-(*m*-methoxyphenyl)-ethanol show almost the same internal interaction in spite of the great distance between σ constants ($\sigma_m = +0.115$, $\sigma_p = -0.268$). Even the correction which will be discussed in

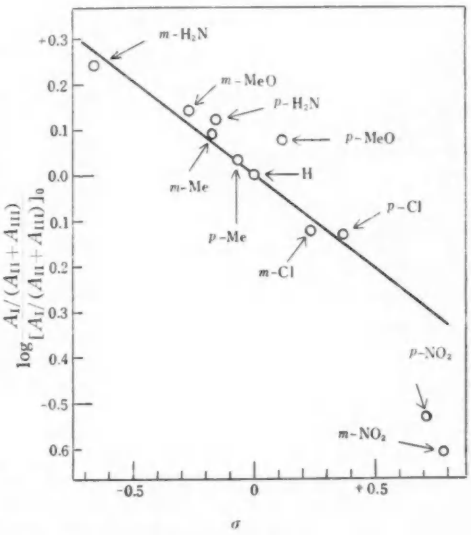


Fig. 4. Relation between $\log \frac{A_I/(A_{II}+A_{III})}{[A_I/(A_{II}+A_{III})]_0}$ in 2-arylethanol and σ constants for structure VIII.

the following paragraph modifies only σ_m but does not affect σ_p. The deviation of 2-(nitrophenyl)-ethanols can be attributed to the error in dividing the apparent curves into three, since the bands I of these compounds are the smallest comprising no maxima nor distinct shoulders.

The relation between the σ constants and $\log \frac{A_I/(A_{II}+A_{III})}{[A_I/(A_{II}+A_{III})]_0}$ for structure IX is shown in Fig. 5. The σ constants for the para-substituted compounds should be the mean values of those for meta and for para and those for the meta-substituted compounds should be expressed by $\left(\frac{\sigma_o+\sigma_p}{2}+\sigma_m\right)\Big/2$. Unfortunately, however, few σ values for ortho-substitution have been known, the only example having been provided by Shulgin and Baker[18]

16) R. S. Mulliken, *J. Chem. Phys.*, **19**, 514 (1951); *J. Am. Chem. Soc.*, **74**, 811 (1952).

17) L. P. Hammett, "Physical Organic Chemistry", McGraw-Hill Book Co., New York (1940), p. 184. Also see: H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

18) A. T. Shulgin and A. W. Baker, *Nature*, **182**, 1299 (1958).

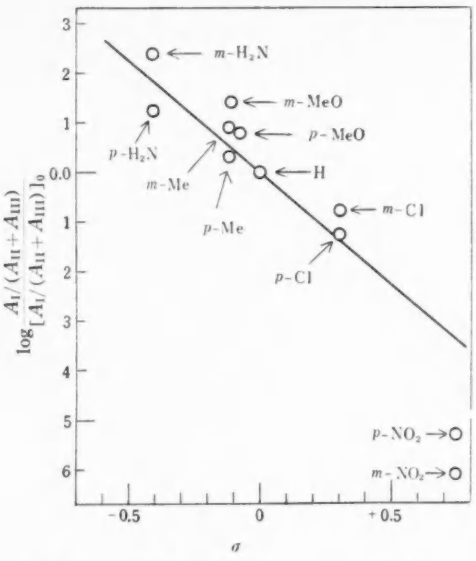


Fig. 5. Relation between $\log \frac{A_I/(A_{II}+A_{III})}{[A_I/(A_{II}+A_{III})]_0}$ in 2-arylethanol and σ constants for structure IX.

who found the same values for ortho-chloro and para-chloro within the experimental error and a slightly more negative value for ortho-methoxyl than for para-methoxyl. Electron densities computed by the molecular orbital method have been reported in some instances and slight differences between ortho- and para-position have been reported, although they do not cover all the substituents used in the present work. Hence, $(\sigma_m+\sigma_p)/2$ is used as an approximation for the substituents in the meta-position except the methoxyl group for which respective values for ortho and for para are available.

There are deviations from a straight line, even though the results are better than those considered from structure VIII. In other words, the meta-substituted 2-phenylethanol is always favored in the internal interaction over the para-substituted, or the former always gives a greater integrated intensity of band I, when an electron-releasing group is introduced. The deviations may be caused by neglecting the electron density of the ortho-position and/or by the contribution of structure VIII to some extent, which favors 2-phenylethanols with an electron-donating group in the meta-position for the interaction. The deviation may be also caused by using $A_{II}+A_{III}$ instead of A_{II} as the integrated intensity of the free form, since the scale model indicates that the free form capable of producing such an interaction is only one, of which integrated intensity is given by A_{II}.

If the intramolecular interaction between the hydroxyl group and the π-electrons is considered as a complex formation between a cation and an aromatic nucleus, structure IX can be supported. Namely, Rundle and Goring[19] observed on the basis of diffraction data that the silver ion in the complex with benzene is bonded equally with the two carbon atoms of the benzene nucleus and is located above the surface. Judged from the present results shown in Table II, the wave number of the ν_{O-H} absorption of the interacting form can be said just the same for a given substituent irrespective of its position. This fact strongly supports structure IX as the internally interacting form of 2-phenylethanol.

Strictly speaking, however, structure VIII can not be totally rejected, because it is one of the possibilities that favor the meta-substituted compounds in the internal interaction more than the para-substituted. Doering et al.[20] studied the structure of the heptamethylbenzenonium compound and postulated the 1,1,2,3,4,5,6-heptamethylbenzenonium ion with C_1 of the tetrahedral structure, without totally rejecting another with the methyl ion located between the two carbon atoms of the benzene nucleus and out of the plane. On the contrary, the present conclusion is that structure IX is the main contribution[21].

3-Arylpropanols.—As the representatives of 3-arylpropanols the ν_{O-H} absorption curves of 3-(*p*-aminophenyl)-propanol and 3-(*p*-chlorophenyl)-propanol and the corresponding divided values are shown in Figs. 6 and 7, respectively. The results are summarized in Table III.

It may be suspected that the lowest

19) R. E. Rundle and J. H. Goring, *J. Am. Chem. Soc.*, **72**, 5337 (1950).

20) W. von Doering, M. Saunders, H. G. Boyton, H. W. Earhart, E. F. Wadley, W. R. Edwards and G. Laber, *Tetrahedron*, **4**, 178 (1958).

21) It may be pointed out that another possibility exists in which either structure VII or VIII contributes. Namely, the direction of the hydroxyl group points to either C_1 or C_2 depending on the favorable electron density on the carbon atom. This is improbable, however, since interacting forms of both meta- and para-substituted compounds absorb at nearly the same wave number, while, in O-H···O hydrogen bonding, ν_{O-H} absorption generally appears at lower wave numer in the formation of a six-membered ring than of a five-membered ring.

TABLE III. ν_{O-H} ABSORPTIONS OF 3-ARYLPROPANOLS (x-$RC_6H_4CH_2CH_2CH_2OH$)

R	x	OH	ν_{max} (cm^{-1})	$\Delta\nu^a_{1/2}$ (cm^{-1})	$A\times10^{-3}$ ($mol^{-1}\cdot l.\cdot cm^{-2}$)	$\Delta\nu_{III-I}$ (cm^{-})	$\Delta\nu_{III-II}$ (cm^{-1})
		I	3587.0	33.0	1.11		
	m	II	3627.2	24.0	2.15	52.9	12.7
		III	3639.9	17.6	3.33		
H_2N		I	3590.0	29.0	0.98		
	p	II	3625.8	20.0	1.92	49.9	14.1
		III	3639.9	16.7	3.32		
		I	3593.0	35.0	0.50		
	m	II	3625.2	24.0	2.28	47.2	15.0
		III	3640.2	16.6	3.62		
CH_3O		I	3595.0	27.0	0.39		
	p	II	3626.8	21.2	2.05	45.0	13.4
		III	3640.2	14.6	2.92		
		I	3593.2	30.6	0.43		
	m	II	3627.0	23.0	1.97	46.8	13.0
		III	3640.0	15.8	2.99		
CH_3		I	3598.0	31.4	0.51		
	p	II	3628.5	22.6	2.23	42.6	12.1
		III	3640.6	15.6	3.01		
H		II	3623.0	21.6	1.93		16.7
		III	3639.9	16.0	3.57		
Cl	*p*	II	3627.8	24.8	2.53		12.6
		III	3640.4	16.6	3.40		

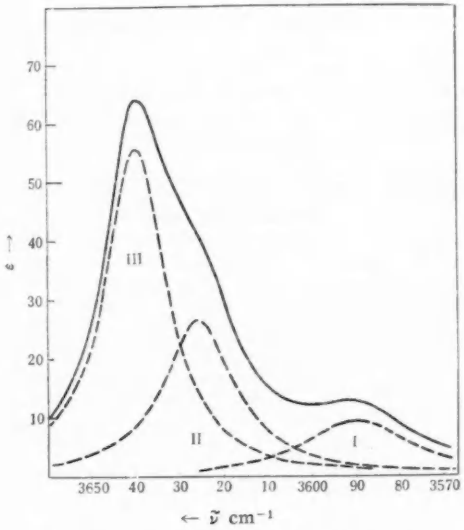


Fig. 6. ν_{O-H} absorption of 3-(*p*-aminophenyl)-propanol.

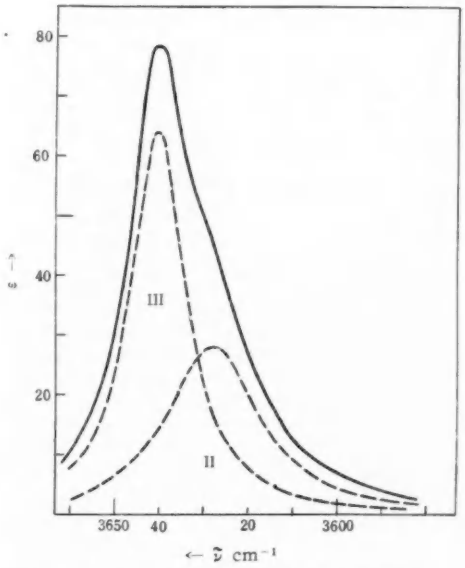


Fig. 7. ν_{O-H} absorption of 3-(*p*-chlorophenyl)-propanol.

ν_{O-H} absorption (band I) of 3-(aminophenyl)-propanols might be the ν_{N-H} absorption, but actually ν_{N-H} absorptions are found at 3479 cm^{-1} and 3393 cm^{-1} for 3-(*m*-aminophenyl)-propanol. The shift in the wave numbers of the ν_{O-H} absorption of the interacting form is consistent with the results obtained with 2-arylethanols. Namely, the methoxyl and the methyl groups give bands I at nearly the same wave number and the amino group further lowers the wave number. The difference between the meta- and the para-substituted compounds can not be taken as an

TABLE IV. ν_{O-H} ABSORPTIONS OF 4-ARYLBUTANOLS (p-$RC_6H_4CH_2CH_2CH_2CH_2OH$)

R	OH	ν_{max} (cm^{-1})	$\Delta\nu^a_{1/2}$ (cm^{-1})	$A\times10^{-3}$ ($mol^{-1}\cdot l.\cdot cm^{-2}$)	$\Delta\nu_{max}$ (cm^{-1})
H_2N	II	3626.1	19.8	2.21	13.0
	III	3639.1	17.4	3.26	
H	II	3626.6	23.2	2.36	13.3
	III	3639.9	17.6	3.43	

important indication, because bands I constitute the smallest peaks and errors involved in dividing the apparent absorption do not allow to discuss such a small difference.

It is apparent that the interaction is less favored in 3-arylpropanols than in 2-arylethanols, because even 3-(aminophenyl)-propanols give the smaller integrated intensities of band I. 3-Phenylpropanol itself does not show any absorption corresponding to band I of the other compounds with an electron-releasing group. However, the close examination of band II reveals that band II of 3-phenylpropanol is located at a rather low wave number, $\Delta\nu_{III-II}$ being as large as 16.7 cm^{-1}, in comparison with 12~15 cm^{-1} of others. It may be attributed to the fact that the peak corresponding to band I of 3-phenylpropanol is too small to be separated from others by the present technique. The above assumption seems verifiable because 3-(p-chlorophenyl)-propanol gives bands II and III in the normal positions for primary alcohols, $\Delta\nu_{III-II}$ being 12.6 cm^{-1}. In this case, the electron-attracting power of the chlorine atom seems to prohibit the interaction from taking place.

It is rather strange that 3-arylpropanols possess smaller numbers of internally interacting molecules even though the interacting form seems to be more stabilized than that in 2-arylethanol, because the wave numbers of bands I of 3-arylpropanols are lower than those of 2-arylethanols[22]. It must be attributed either to the unfavorable change in entropy and energy or to the difference in nature, as the authors pointed out for allyl alcohol and 3-buten-1-ol[3]. In this case, however, the present authors will choose the former for the following reasons. Firstly, the electronic effect in 3-arylpropanols shows the same trend as that in 2-arylethanol, and, secondly, the interacting form in 3-arylpropanol requires the all-*gauche* form including two carbon and one oxygen atoms, while that in 2-arylethanol requires the *gauche* form including one each of carbon and oxygen atoms. Hence, even though the interacting form of 3-arylpropanols will be more stabilized, if once formed, the unfavorable change in entropy and energy will limit the number of the molecules.

As to the nature of the interaction, 3-arylpropanols do not provide further information. The authors again come to a difficulty because of the weakness of bands I, but would like to assign tentatively the same structure as 2-arylethanols, because the meta- and the para-substituted compounds give nearly the same ν_{O-H} absorptions.

4-Arylbutanols.—The results of 4-arylbutanols are shown in Table IV.

From Table IV, it is obvious that 4-phenylbutanol does not possess any intramolecular interaction between the hydroxyl group and the π-electrons, since its ν_{O-H} absorption is normal for primary alcohols. Even 4-(p-aminophenyl)-butanol shows the normal absorption for primary alcohols in spite of the favorable electron density on the aromatic nucleus due to the presence of the strongly electron-releasing amino group. And again, this fact must be attributed to the unfavorable change in both entropy and energy.

Thus, it can be concluded that the internal interaction between the hydroxyl group and the π-electrons of the benzene nucleus occurs, when the hydroxyl group is an alcoholic O-H and the carbon chain is not fixed, up to 3-phenylpropanol in the series of ω-arylalkanols.

Summary

The electronic effect on the intramolecular interaction between the hydroxyl group and the π-electrons of the benzene nucleus was studied with various ω-arylalkanols. In 2-arylethanols, introduction of an electron-releasing group into the benzene nucleus gives rise to the shift of the ν_{O-H} absorption maxima to a lower wave number and to greater integrated

22) For example, see R. M. Badger and S. H Bauer, *J. Chem. Phys.*, 5, 839 (1937).

intensities of the band due to the interacting form, and introduction of an electron-attracting group to a higher wave number and smaller integrated intensities. However, the wave number of the band due to the interacting form is not affected by the position of the substituent, as far as the substituent is the same. Thus, the structure represented by IX is favored. On the other hand, a compound with an electron-releasing group in the meta position always shows greater integrated intensities of the band due to the interacting form than the para-substituted isomer and this fact saves structure VIII from entire rejection. Hence, the authors tentatively assign structure IX as the most favorable with participation of structure VIII to some extent.

In 3-arylpropanols the interaction is observed only in the compounds with an electron-releasing group and 3-(*p*-chlorophenyl)-propanol shows the normal ν_{O-H} absorption for primary alcohols. The phenomenon that 3-arylpropanols show smaller interaction in spite of the appearance of the band due to the interacting form at a lower wave number is attributed to the unfavorable change in both energy and entropy.

In 4-arylbutanol no interaction is observed, even though a strongly electron-donating group is introduced.

Thus, as the authors predicted, it has been proved that the intramolecular interaction occurring in 2-phenylethanol is different in nature from that in benzyl alcohol.

The authors wish to express their hearty thanks to Professor Y. Urushibara and Professor T. Shimanouchi for their valuable suggestions and discussions. The authors are also indebted to the Ministry of Education for a Grant in Aid for Fundamental Scientific Research.

Department of Chemistry
Faculty of Science
The University of Tokyo
Hongo, Tokyo

Self-diffusion of Iodide Ion and Strontium Ion in Strontium Iodide Solutions

By Ryohei MATUURA and Yasushi KOGA

(Received April 3, 1959)

Self-diffusion coefficients of iodide ion in hydrogen iodide, sodium iodide, potassium iodide and rubidium iodide solutions were measured by Mills and Kennedy[1]. They showed that in every iodide solution studied the product of self-diffusion coefficient of iodide ion and relative viscosity of the solution, i.e., $D\eta/\eta_0$, was linear against the square root of the concentration, $\sqrt{c}$, up to considerably high concentrations. In the case of self-diffusion of sodium, potassium, chloride and sulfate ions, however, no such linear relations were found. Matuura and Shimozawa[2] showed that the self-diffusion of calcium and strontium ions in chloride solutions was very complicated with respect to the concentration of the solution and found that the $D\eta/\eta_0$ vs. $\sqrt{c}$ curves had two minima and one maximum. The important difference of iodide ion from the other ions cited above in connection with the kinetic behaviors in aqueous solutions may be in its large size and poor hydration. A simple picture of the self-diffusion process for such "unhydrated" ions was suggested by Mills and Kennedy, which, in the case of monovalent counter ions, seems to explain the iodide ion self-diffusion satisfactorily. It is very interesting to investigate whether or not the same picture could be extended to the iodide of the divalent counter ions. The present work has been performed with the solution of strontium iodide in order to check this point and to obtain further knowledge

1) R. Mills and J. W. Kennedy, *J. Am. Chem. Soc.*, **75**, 5696 (1953).
2) R. Matuura and R. Shimozawa, *Mem. Faculty of Science, Kyushu University, Ser. C*, **2**, 53 (1955).

of the behavior of ions in electrolyte solutions.

Experimental

Apparatus. — The diffusion apparatus was essentially the same as that proposed by Anderson and Saddington[3] and modified by Wang[4]. The schematic diagram of the apparatus is shown in Fig. 1. A three-necked flask of one liter capacity

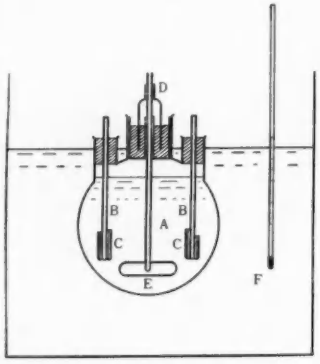


Fig. 1. Diffusion apparatus.

(A) was fitted with capillary holders (B) and a mercury seal stirrer (D). A plastic paddle (E) was turned slowly by an electric motor. The flask and contents were immersed in a thermostat (F) of 25±0.01°C. The capillary diffusion cells (C) were prepared as follows. The different diameter capillaries of Pyrex glass were used and the inside diameter was calibrated by filling with pure mercury. They were 0.0612 and 0.0780 cm. The capillaries were cut to different lengths and the top end of each capillary was ground flat with fine carborundum. The other end was sealed with glass to make a flat bottom. The length of each capillary was measured precisely with a micrometer caliper. These lengths varied from 2.97 to 5.19 cm.

Procedure.—Capillaries were filled with a radiotracer solution of known concentration by using a fine pipette drawn from a glass tubing. They were then held vertically in a flask containing one liter of inactive strontium iodide solution of the same concentration as the capillary solution. The air above the solution in the flask had been replaced by nitrogen gas so that the strontium iodide solution might not be decomposed by oxygen in air. Also, in order to avoid the effect of light, the outer surface of the flask had been coated with black paint. Each capillary was immersed in the flask solution up to just below the upper end of the capillary and left standing for about 30 min. in order to secure thermal equilibrium between the solution inside and outside of the capillary. Then the capillaries were dipped completely into the flask solution and the diffusion was allowed to start. The nitrogen gas in the flask was renewed after setting the capillary cells in it. During the diffusion period the flask solution was stirred by turning a paddle (see Fig. 1) at a constant rate 90 r. p. m. This turning rate was chosen in order to minimize the Δl correction according to Mills and Kennedy[1]. After each diffusion period (3 to 7 days) the capilliaries were taken out of the flask and the radioactivity of the solution in each capillary was measured by a counter. The radioactivity of the original solution was also measured at the same time and two values of radioactivity, that is, before and after diffusion corrected for natural decay, was compared on the same volume unit.

The viscosity of the solution was measured with an Ostwald viscometer at 25°C.

Materials. — The tracers used in the present experiment were ^{131}I and ^{89}Sr. ^{131}I (half-life 8.0 days) was obtained in the form of chloride in weak basic sodium bisulfite solution. The bisulfite was removed by titration with hydrogen iodide to a pH of about 5. A drop of this solution was added to a quantity of strontium iodide solution. The concentration of iodide in this solution was measured volumetrically. Since the concentration of cations other than strontium in this solution was negligibly small, this was used as a tracer solution for iodide ion diffusion in strontium iodide solutions. The radioactivity of ^{131}I in the solution was measured by a proportional gas counter.

^{89}Sr (half-life 54 days) was obtained as a carrier-free chloride. This contained less than 10% ^{90}Sr (half-life 25 years) which decays into ^{90}Y (half-life 65 hr.). A drop of the original solution was dried up and dissolved in the strontium iodide solution of known concentration to make a capillary solution. After diffusion the solution was drawn out of a capillary by means of a fine pipette. The capillary was washed several times with a large excess of distilled water. The sample solution, together with all washings, was evaporated to dryness and its radioactivity (c_{av}) was measured by a G. M. counter. The radioactivity (c_0) of the original solution was also measured at the same time. It was found that the ratio c_{av}/c_0 depended upon the duration after the diffusion had been stopped, because of the destruction of equilibrium between ^{90}Sr and ^{90}Y caused by the difference in the diffusion rate of the two species. So the measurement of c_{av} and c_0 was made week by week until the constant value of c_{av}/c_0 was obtained. It took two to four weeks to attain the complete equilibrium between ^{90}Sr and ^{90}Y. From this constant value of c_{av}/c_0 the diffusion coefficient of strontium ion in strontium iodide solutions was calculated.

It was found that strontium iodide decomposes gradually in air and by light, resulting in the liberation of iodine which makes the solution colored. So it was necessary to use a fresh sample for each experiment. The strontium

3) J. S. Anderson and K. Saddington, *J. Chem. Soc.*, **1949**, S 381.
4) J. H. Wang, *J. Am. Chem. Soc.*, **73**, 4181 (1951).

iodide solution was prepared from strontium carbonate and hydrogen iodide just before each run of diffusion and viscosity measurement. Rigorous precautions were made for the solution not to change by air and light during the experiment, as already mentioned. The solution was slightly acidic. Its concentration was determined gravimetrically as strontium sulfate and also volumetrically as silver iodide. Both methods agreed well.

Calculations

Under the present experimental conditions the Fick's diffusion equation is solved as follows[5].

$$\frac{c_{av}}{c_0} = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left[-(2n+1)^2 \pi^2 Dt/4l^2\right] \tag{1}$$

where, c_{av} is the average concentration of the tracer ion in the capillary solution after diffusion, c_0 is its initial concentration, l is the length of the capillary, t is the diffusion time and D is the self-diffusion coefficient. For the value of Dt/l^2 greater than 0.2 the series in the Eq. 1 converges so rapidly that all terms following the first can be neglected with an error smaller than 0.2%. This condition was always kept in the present experiment. Thus the equation

$$2.303 \log \frac{\pi^2}{8} \cdot \frac{c_{av}}{c_0} = -\frac{\pi^2 Dt}{4l^2} \tag{2}$$

was always used for the calculation of the self-diffusion coefficient of iodide ion and strontium ion in the strontium iodide solutions.

Table I. Self-diffusion coefficient of iodide ion in strontium iodide solutions at 25°C

c (mol. SrI_2/l.)	$D_{I^-} \times 10^5$ (cm²/sec.)
0.00042	1.995±0.03
0.0024	1.991±0.02
0.0042	1.928±0.02
0.0111	1.869±0.03
0.0128	1.881±0.02
0.0138	1.880±0.03
0.056	1.841±0.03
0.187	1.791±0.02
0.223	1.76 ±0.03
0.375	1.694±0.02
0.438	1.663±0.01
0.713	1.613±0.04

Results

Self-diffusion coefficients of iodide ion and strontium ion in strontium iodide solution of various concentrations are shown in Tables I and II, respectively.

Table II. Self-diffusion coefficient of strontium ion in strontium iodide solutions at 25°C

c (mol. SrI_2/l.)	$D_{Sr^{2+}} \times 10^5$ (cm²/sec.)
0.0038	0.788±0.002
0.0116	0.744±0.003
0.0125	0.762±0.012
0.0242	0.748±0.013
0.096	0.743±0.010
0.0985	0.734±0.003
0.2197	0.719±0.02
0.500	0.704±0.018
0.7245	0.681±0.008
0.985	0.630±0.017

Values of relative viscosity of strontium iodide solutions at 25°C are shown in Table III.

Table III. Relative viscosity of strontium iodide solutions at 25°C

c (mol. SrI_2/l.)	η/η_0
0.001	0.995
0.01	0.993
0.1	1.012
0.2	1.033
0.4	1.059
0.6	1.096
0.8	1.139
1.0	1.186
1.2	1.248
1.4	1.322
1.6	1.391
1.8	1.469
2.0	1.588
2.2	1.741
2.4	1.884

Discussion

In the dilute solution the self-diffusion of an ion is mainly controlled by the relaxation of ionic atmosphere around the ion. On the basis of Onsager's limiting law for the diffusion coefficient[6], Gosting and Harned[7] derived an equation for the variation of self-diffusion coefficient of the ion with its concentration, which in the case of self-diffusion of the ion (chemical

5) A. C. Wahl and N. A. Bonner, "Radioactivity Applied to Chemistry", John Wiley & Sons, Inc., New York (1951), p. 77.

6) L. Onsager, *Ann. N. Y. Acad. Sci.*, **46**, 241 (1945).

7) L. J. Gosting and H. S. Harned, *J. Am. Chem. Soc.*, **73**, 159 (1951).

species 1) in its binary electrolyte (chemical species 1 and 2) solutions, may be put into the following form.

$$D_1=\frac{RT\lambda^0_1}{|Z_1|F^2}-2.694\times10^{16}\frac{\lambda^0_1|Z_1|F}{3N\varepsilon}\sqrt{\frac{4\pi}{\varepsilon RT}}\times\left(1-\sqrt{d(\omega_1)}\right)\sqrt{\sum_i c_i Z_i^2} \quad (3)$$

where, D_1 is the self-diffusion coefficient of the ion (in cm²/sec.), Z_1 and λ^0_1 are its number of the charge and limiting equivalent conductance (in coulomb/sec.×cm²/V.), respectively, c_i is the concentration of the i-th ion (in mol./l.), ε is dielectric constant of the solvent, and R, F, N and T are gas constant (in joule/deg. mol.), Faraday constant (in coulomb), Avogadro number and absolute temperature, respectively. $d(\omega_1)$ in Eq. 3 is given by

$$d(\omega_1)=\left(\frac{|Z_1|}{|Z_1|+|Z_2|}\right)\left(\frac{1}{2}+\frac{|Z_2|\lambda^0_2}{|Z_2|\lambda^0_1+|Z_1|\lambda^0_2}\right) \quad (4)$$

For the self-diffusion of iodide ion and strontium ion in strontium iodide solutions we use[8]

$$\lambda_{I^-}=76.8$$
$$\lambda_{Sr^{2+}}=59.46$$

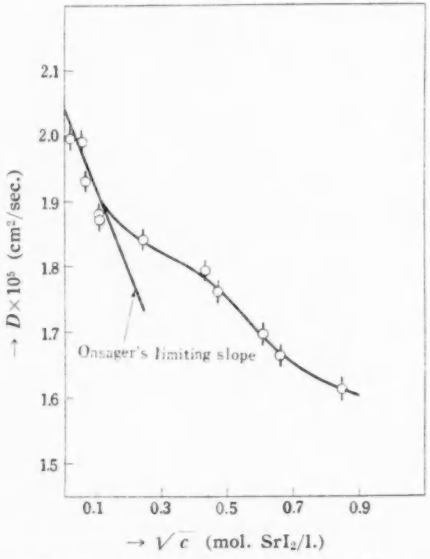


Fig. 2. Self-diffusion coefficient of I^- in SrI_2 solutions against square root of the concentration at 25°C.

8) D. A. McInnes, "The Principles of Electrochemistry", Reinhold Publishers Corp., New York (1950), p. 342.

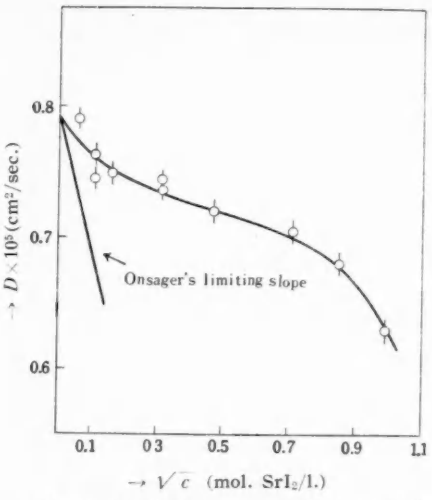


Fig. 3. Self-diffusion coefficient of Sr^{2+} in SrI_2 solutions against square root of the concentration at 25°C.

and we obtain the following equations by inserting the numerical values in Eq. 3:

$$D_{I^-}\times10^5=2.045-1.12\sqrt{c} \quad (5)$$

$$D_{Sr^{2+}}\times10^5=0.792-1.04\sqrt{c} \quad (6)$$

where, c is expressed in mol. SrI_2/l. These are limiting laws for the self-diffusion in the present case. In Figs. 2 and 3 are shown measured D_{I^-} and $D_{Sr^{2+}}$ against $\sqrt{c}$, respectively. It is seen that the experimental data fit the limiting law fairly well.

At higher concentrations the situation is much more complicated. Of various factors which control the ionic self-diffusion three may be considered most important, i.e., the viscosity of the solution, the hydration of the diffusing ion (i.e., the interaction between ion and solvent) and the state of ionic atmosphere (i.e., the interaction between ions). The correction for viscosity of the solution is usually made simply by multiplying D with η/η_0. In Fig. 4 $D\eta/\eta_0$ for iodide ion is plotted against $\sqrt{c}$. The curve for iodide ion is approximated by two straight lines. The straight line of lower concentrations can be extrapolated exactly to the Nernst limiting value, D_0, while that of higher concentrations gives a lower value by extrapolation to the zero concentration. Mills and Kennedy[1] showed that the $D\eta/\eta_0$ vs. $\sqrt{c}$ relation for iodide ion in the solution of iodide of monovalent

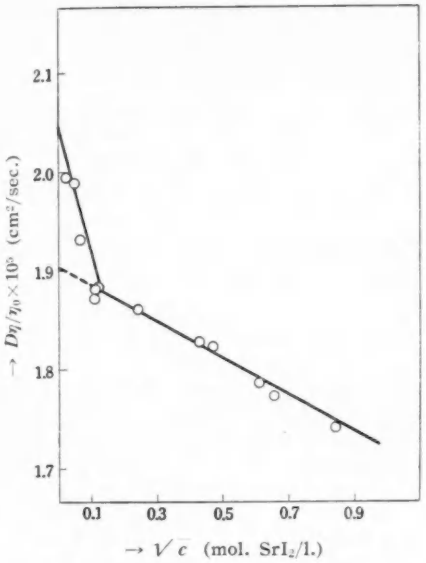


Fig. 4. $D\eta/\eta_0$ vs. $\sqrt{c}$ relation for I^- in SrI_2 solutions at 25°C.

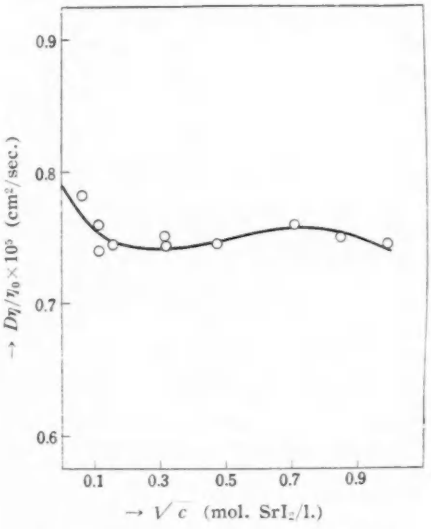


Fig. 5. $D\eta/\eta_0$ vs. $\sqrt{c}$ relation for Sr^{2+} in SrI_2 solutions at 25°C.

metal or hydrogen is linear all through from low to considerably high concentrations and extrapolated to the Nernst limiting value. It is not perfectly evident why the self-diffusion of iodide ion in strontium iodide is markedly different from that in the iodides which Mills and Kennedy studied, but one might ascribe it to the difference in the state of ionic atmosphere around the diffusing iodide ion.

The $D\eta/\eta_0$ vs. $\sqrt{c}$ relation for strontium ion in the solution of strontium iodide is shown in Fig. 5. This curve is much more complicated than and quite different in nature from the curve for iodide ion. It is well known that strontium ion is strongly hydrated, while iodide ion is "unhydrated". Matuura and Shimozawa[2] applied an empirical equation to the self-diffusion of strongly hydrated ions, which is

$$D\eta/\eta_0 = D_0 - k_1\sqrt{c} + k_2 c \log c + k_3 c \qquad (7)$$

where, k_1, k_2 and k_3 are constants. Of these k_1 is a limiting slope $D\eta/\eta_0$ vs. $\sqrt{c}$ relation and can be calculated from Fig. 5. Eq. 7 may be checked by plotting

$$F(D) \equiv \frac{D\eta/\eta_0 - D_0 + k_1\sqrt{c}}{c} \qquad (8)$$

against $\log c$. In Fig. 6 this plot is shown. It is seen that Eq. 7 is a fair expression for the self-diffusion of strontium ion in strontium iodide solutions.

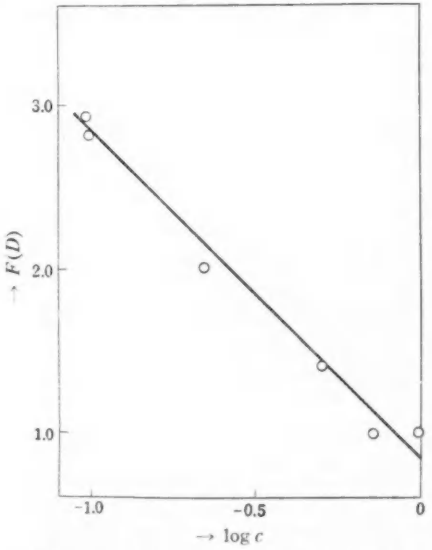


Fig. 6. $F(D)$ vs. $\log c$ relation for Sr^{2+} in SrI_2 solutions.

From the straight line in Fig. 6 the values of k_2 and k_3 are calculated as shown in Table IV. In the same table the data are given for the self-diffusion of strontium ion in strontium chloride

solutions and of sodium ion in sodium iodide and sodium chloride solutions[2].

TABLE IV. VALUES OF k_2 AND k_3 FOR STRONTIUM AND SODIUM ION

System	k_2	k_3
Sr^{2+} in SrI_2	−1.98	0.84
Sr^{2+} in $SrCl_2$	−1.54	0.93
Na^+ in NaI	−0.67	0.24
Na^+ in NaCl	−0.51	0.35

It is clear from Table IV that the absolute values of both k_2 and k_3 are larger for strontium ion than for sodium ion. Since Eq. 7 is an empirical one, the physical meaning of k_2 and k_3 is not definitely given, but one may conclude that k_2 and k_3 are mainly concerned with the charge (and of course also with the hydration) and size of the diffusing ion.

Summary

The self-diffusion coefficient of iodide ion and strontium ion in aqueous strontium iodide solutions has been measured by a capillary method. It has been found that the Onsager's limiting equation can be applied to the self-diffusion of both ions. The $D\eta/\eta_0$ vs. $\sqrt{c}$ relation for iodide ion has been represented by two straight lines, while that for strontium ion has been shown by a much more complicated curve. The latter has been represented successfully by an empirical equation for strongly hydrated ions presented by Matuura and Shimozawa.

A part of this work was performed at the Department of Chemistry, Washington University, St. Louis, Mo., U. S. A. The authors wish to express their thanks to Professor Joseph W. Kennedy of Washington University for his kind advice and encouragement.

Department of Chemistry
Faculty of Science
Kyushu University
Hakozaki, Fukuoka

SHORT COMMUNICATIONS

*Infrared Spectra of Polyvinyl Chloride**

By Akihiro KAWASAKI, Shigeo SHIOTANI, Junji FURUKAWA and Teiji TSURUTA

(Received June 10, 1959)

There exist many reports on infrared spectra of polyvinyl chloride, but are found only a few studies[1-5] which deal with crystalline and amorphous bands in the infrared spectra of this polymer.

With respect to some samples of polyvinyl chloride, we have examined correlation between the specific gravity and the optical density in the absorption bands ranging from 4,000 to 700 cm^{-1}.

Polyvinyl chloride was prepared at room temperature with a binary mixture of triethylaluminum and di-*tert*-butyl peroxide as catalyst. The viscosity average molecular weight of the polymer was 32,000. The samples were in the form of thin solid films, which were prepared from tetrahydrofuran solution of the polymer. By heat treatment in the Wood alloy, the specific gravity, d_4^{30}, of the sample was controlled from 1.3887 to 1.4022.

The examination of the infrared spectra of the polymer having various specific gravity has made clear that the ratios of any two of the optical densities at 2920, 1375 and 1092 cm^{-1} remain almost unchanged irrespective of the change in the specific gravity of the samples. Since it was considered, from this result, that each of the bands mentioned above varied in the same way with the specific gravity, the band at 2920 cm^{-1} was taken as standard and the ratio of optical densities at every absorption band to 2920 cm^{-1} band was calculated.

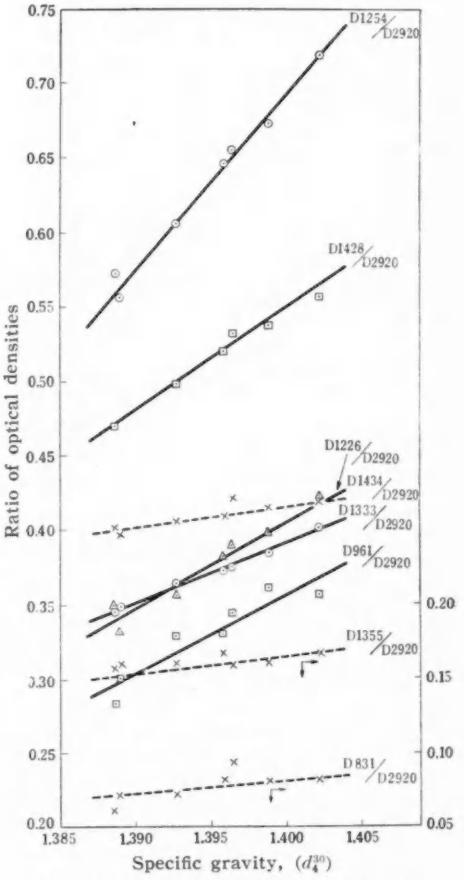


Fig. 1. Relation between optical density and specific gravity.

The liner relationship in Fig. 1 between the specific gravity and the optical density at bands 1428, 1333, 1254, 1226 (distinct parallel band) and 961 cm^{-1}, and the differential absorption band between two polymers having different specific gravity in Fig. 2 lead to the conclusion that these five absorption bands correlate with the specific gravity or crystallinity of the sample. A similar relation was observed

* Presented before the Symposium on Raman and Infraed Spectra at Kyoto, October 16, 1958.

1) S. Krimm and C. Y. Lang, *J. Polymer Sci.*, **22**, 95 (1956).

2) R. J. Grisenthwaite and R. F. Hunter, *Chem. & Ind.*, **1958**, 719.

3) S. Mizushima, T. Shimanouchi and S. Tsuchiya, Abstract of the Paper read in the 11th Annual Meeting of the Chemical Society of Japan, Tokyo (1958), p. 147.

4) S. Mizushima, T. Shimanouchi and S. Tsuchiya, Abstract of the Paper read in the Sympsoium on High Polymer, Osaka (1958), p. 127.

5) H. Watanabe and T. Hotta, Abstract of the paper read in the Symposium on High Polymer, Nagoya (1957), p. 54.

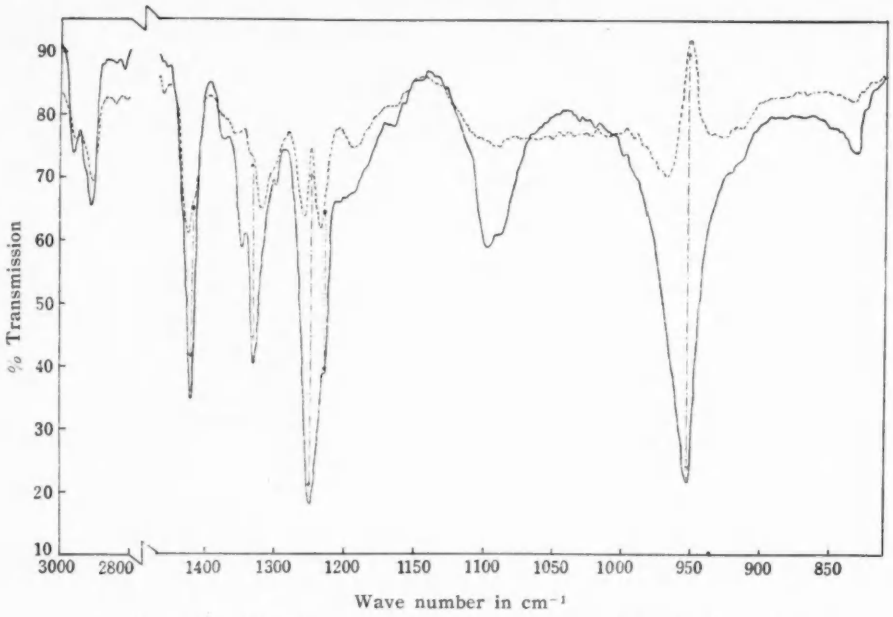


Fig. 2. Differential infrared spectra (——: reference, lower density polymer, ----: reference, higher density polymer.)

also in the absorption bands at 1434, 1355 and 831 cm^{-1} but its dependency upon the specific gravity was much smaller than the above case.

The analysis of these results is under study in our laboratory. Full dentails will be reported in this bulletin.

The authors wish to express their gratitude to Dr. H. Tadokoro, Faculty of Science, Osaka University, and to Dr. Z. Kumazawa, Faculty of Agriculture, Kyoto University, for advice and kindness in infrared analysis.

Department of Industrial Chemistry
Faculty of Engineering
Kyoto University
Sakyo-ku, Kyoto

Infrared Spectra of Crystalline and Amorphous Polystyrene

By Masatami TAKEDA, Kazuyoshi IIMURA
Akira YAMADA and Yoshio IMAMURA

(Received June 30, 1959)

It has been reported[1] that crystalline polystyrene (CPS) prepared by Ziegler type catalyst shows a quite different infrared spectrum from that of amorphous polystyrene (APS) prepared by radical catalyst. It has been also suggested[2] that some bands in the spectrum of CPS could be associated with the three fold herical structure[3] of isotactic polystyrene.

We have studied the infrared spectrum of CPS-I* in the solid state, in the solution of carbon disulfide***, and in the molten state, and have compared them with the corresponding spectra of APS**. Another

1) G. Natta, *Makromol. Chem.*, **16**, 213 (1955).
2) H. Tadokoro et al., This Bulletin, **32**, 313 (1959).
3) C. W. Bunn and E. R. Howelles, *J. Polymer Sci.*, **18**, 307 (1955).

* Prepared by Ziegler catalyst and separated from insoluble parts with cold methyl ethyl ketone after treating with *n*-heptane.

** Commercial polystyrene, "Styron-666".

*** The solution was prepared by extraction of CPS-I at the boiling point of carbon disulfide.

crystalline polystyrene, CPS-II****, prepared by Alfin catalyst has been studied in the solid state.

The spectra of these samples in various states are shown in Fig. 1. The most remarkable differences between CPS-I and APS in solid are found in the bands at 1085, 1054 and 567 cm^{-1}. These absorption bands of CPS-I in solution are very similar to those of solid CPS-I, but some of the other bands observed in the solid state disappear.

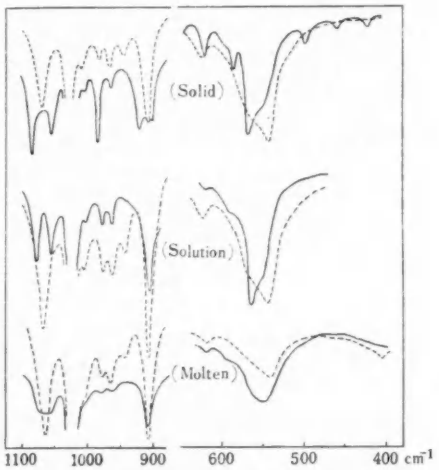


Fig. 1. Infrared spectra of CPS-I and APS in various states.
—— CPS-I ---- APS

In the molten state, the spectrum of CPS-I is almost similar to the spectrum of APS, except for the following points: the doublet at 1085 and 1054 cm^{-1} of solid CPS-I changes into a single and broad band with the maximum at 1070 cm^{-1} with melting, whereas molten APS shows a rather sharp absorption at 1070 cm^{-1}.

The asymmetric band with the maximum at 567 cm^{-1} of solid CPS-I becomes a symmetric and broad band with the maximum at 552 cm^{-1}, while the absorption maximum of molten APS at 543 cm^{-1} remains unchanged.

The observed absorption frequencies are shown in Table I. Complete assignment of the bands at 1085, 1054 and 567 cm^{-1} in both polystyrenes in various states are not yet obtained.

However, the differences between the spectra of CPS-I in various states can be used to classify the observed bands in three groups.

TABLE I. FREQUENCIES IN VARIOUS STATES OF CPS AND APS

CPS-I			APS	
solid	soln.	molten	solid, soln., molten	Classification of the band
1364	1364	1370 w	1370	B
1314	1314	1314 w	1312	B
1297	1297	1295 w	1295	B
1185	1190	1185 w	1182	B
1085	1080			C
		1063 b	1070 s	C
1054	1057			C
984	978 w	978 w	980	A
965	963	963	965	
			945	
923				A
910	908	905	905	
901				A
620 s	620 b	620 b	620 b	A
587				A
567	560			C
		552 b		C
			543	C
499				A
465				A
426				A

s: sharp
b: broad
w: weak in solution and in molten state

(A) Under the first group come the bands at 984, 923, 901, 620, 587, 499, 465 and 426 cm^{-1}. They disappear instantly or are very much weakened when CPS-I dissolves in solution or melts. These bands, which are not observed in the spectrum of APS, may be assigned to the vibrational bands caused by the perturbation by rather long range intra- and intermolecular interactions in the CPS-I crystal. The band at 984 cm^{-1} is considered as a typical crystalline band by Tadokoro et al[4].

(B) Under the second group come the bands at 1365, 1314, 1297 and 1185 cm^{-1}. They are stronger in crystallized CPS-I than in quenched one, and persist in the spectrum of the solution. These bands have been assigned[2] to the CH or CH_2 deformation vibrations, which are closely associated with the intramolecular interaction in the herical chain having a three-fold screw axis.

(C) The doublet at 1085~1054 cm^{-1} and

**** Separated from insoluble parts in cold methyl ethyl ketone after treating with *n*-heptane.

4) H. Tadokoro et al., Symposium of High Polymer, Osaka, Oct., 1958.

the asymmetric bands at 567 cm^{-1} in solid CPS-I and at 543 cm^{-1} in APS could form the third group, because they appear differently in the spectra of molten CPS-I and APS.

The band at 567 cm^{-1} is tentatively assigned by the following reason: The Raman band at 558 cm^{-1} of APS has been assigned to the ν_{6A} mode, an in-plane vibration of benzene nuclei of A_1 mode, by Liang and Krimm[5], which derives from a Raman active and infrared inactive mode of benzene. If all the phenyl radicals in the herical conformation of a polystyrene molecule vibrate in the same phase in the ν_{6A} mode, the dipole moment of the molecule changes along the screw axis of the conformation. It is possible in this case that the ν_{6A} mode is infrared active and shows parallel dichroism which is actually found in our experimental data shown in Fig. 2. Thus we may expect that the band at 567 cm^{-1} is an *X*-sensitive vibration of monosubstituted benzene[6], and sensitive to the short range interaction between the phenyl group and the herical C-C main chain which has alternate *trans* and *gauche* conformations[7].

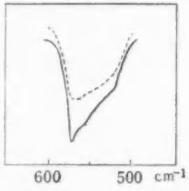


Fig. 2. Dichroism of the 567 cm^{-1} band in solid CPS-I.
—— Electric vector parallel to elongation
---- Electric vector perpendicular to elongation

The band at 543 cm^{-1} of APS is assigned to an *X*-sensitive vibration which is affected by another short range interaction between the phenyl group and the C-C main chain of APS which may have mainly *trans-trans* conformation sequence in their syndiotactic parts.

The doublet at 1085~1054 cm^{-1} of CPS-I and singlet at 1070 cm^{-1} of APS are probably assigned also to the same type of vibration.

On the basis of the above empirical classification of characteristic bands of CPS-I and APS, as a possible interpretation of the origin of these absorption bands, the following tentative conclusions are drawn.

Based on the behavior of C class band, the conformation of CPS-I along the C-C main of a few monomer units seems to differ from that of APS in their molten states. This may lead us to expect that the change of the bands at 1085, 1054 and 567 cm^{-1} must be connected with the content of the isotactic configuration of CPS-I. If this is assumed, it should be suggested that the isotactic contents in the chain configuration of CPS-II is smaller than that of CPS-I, since the C band of CPS-II in the solid state is quite similar to that of molten CPS-I as is shown in Fig. 3.

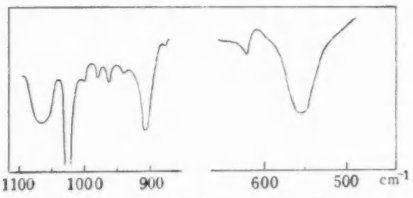


Fig. 3. Infrared spectrum of solid CPS-II.

In solution, it is interesting to note that the herical conformation of isotactic polystyrene is partly reserved, because the persistence of the bands at 567, 1085, 1054 and also 1364, 1314, 1297, 1185 cm^{-1} of crystallized CPS are well recognized.

The authors are grateful to Professor T. Shimanouchi of the University of Tokyo for his discussion and kind cooperation in the measurement of dichroism.

Tokyo College of Science
Kagurazaka, Shinjuku-ku
Tokyo

5) C. Y. Liang and S. Krimm, *J. Polymer Sci.*, **27**, 241 (1958).
6) D. H. Whiffen, *J. Chem. Soc.*, **1956**, 1350.
7) W. R. Krigbaum, D. K. Carpenter and S. Newman, *J. Phys. Chem.*, **62**, 1586 (1958).

On Miyaconitine and Miyaconitinone

Shichiro KAKIMOTO, Nobukatsu KATSUI and Yoshiyuki ICHINOSE

(Received August 7, 1959)

In an earlier paper[1], the extended formulae of miyaconitine(I) $C_{23}H_{29}O_6N$ and miyaconitinone(II) $C_{23}H_{27}O_6N$ were given respectively as follows:

(I) $C_{19}H_{20}(OAc)(OH)(=O)_3(N\text{-}Et)$

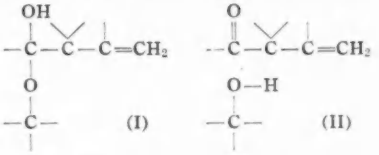
(II) $C_{19}H_{19}(OAc)(=O)_4(N\text{-}Et)$

The present communication presents further consideration of the empirical and extended formulae of I and II:

(I) $C_{24}H_{31}O_6N$: $C_{20}H_{22}(OAc)(OH)(-O-)\cdot(=O)_2(N\text{-}Et)$. λ_{max}^{EtOH} 295 mμ (log ε 1.6), ν_{max}^{KBr} 3470(OH), 1726, 1678(CO), 3090, 1648, 877 cm^{-1} (>C=CH_2)

(II) $C_{24}H_{31}O_6N$: $C_{20}H_{22}(OAc)(OH)(=O)_3\cdot(N\text{-}Et)$. pK_a' 6.5 λ_{max}^{EtOH} 290 mμ(log ε 2.6), ν_{max}^{KBr} 3410(OH) 1728, 1715, 1676(CO), 3090, 1648, 883 cm^{-1} (>C=CH_2)

The presence of the terminal methylene group was confirmed not only by the observation of infrared spectra, but also by ozonolysis and novel Lemieux oxidation[2] to give formaldehyde. Compound I showed extreme susceptibility to aldehyde reagents (viz., Fehling, Tollens and TTC, etc.), but II did not. The oxidation of I with bismuth oxide in refluxing acetic acid yielded II. The infrared spectrum of II showed a band at 3410 cm^{-1} probably due to a tertiary hydroxyl group. These observations are explained by the consideration that the conversion of I to II is not a simple oxidation of a secondary hydroxyl group to a carbonyl group but is an oxidation of a hemiketal moeity existing in I. Ultraviolet absorption of II and its alkamine, miyaconinone(III), $C_{22}H_{25}O_5N$ showed abnormal intensity due to a β,γ-unsaturated carbonyl group[3]: λ_{max}^{EtOH} 294 mμ (log ε 2.6), ν_{max}^{Nujol} 3460, 3310 (OH) 1724, 1673 (CO) 1649, 888 cm^{-1} (>C=CH_2). Therefore, the partial structures of I and II may be represented by the following schemata.



Alkaline hydrolysis of II gave ψ-miyaconinone*(IV), m. p. 254~256°C, $[\alpha]_D^{20}$ −1.0°, pK_a 4.2, λ_{max}^{EtOH} 284 mμ(log ε 1.2). ν_{max}^{Nujol} 3600, 3510 (OH) 1783, 1727(CO) 1648, 889 cm^{-1} (>C=CH_2) (*Anal.* Found: C, 68.58, H, 7.48. Calcd. for $C_{22}H_{25}O_5N$: C, 68.19; H, 7.54%). This compound was obtained also by alkaline treatment of III. In the ultraviolet absorption of IV, the maximum displayed no longer the abnormal intensity as shown in those of II and III. On the other hand, the infrared spectrum of IV showed three peaks due to hydroxyl group although that of III had two peaks. Then it is considered that the reaction of II to IV involves the base-catalyzed conversion of the carbonyl group to a hydroxyl group. A plausible explanation of this reaction is that the carbonyl group showing abnormal intensity in II or III has undergone an internal aldol condensation. It has been previously reported that an α-diketone group adjacent to the nitrogen atom is present[4]. Accordingly, the condensation must have occurred in the methylene group adjacent to the α-diketone. The lower basicity of IV also supports these considerations.

In the titrations of periodate and lead tetraacetate, III and IV took up rapidly one mole more than II in one hour. It is suggested then that III and IV have a vicinal glycol system.

The composition of the fundamental base, $C_{20}H_{31}N$, and the exsistence of terminal methylene group suggest that I and II may be belonged to atisine or garryine type alkaloids.

Furthermore, it has been already reported that songorine[3b,5], one of aconite alkaloids, has the same β,γ-unsaturated ketonic system with II. And so it is considered tentatively that I and II have

1) H. Suginome, S. Furusawa, Y. Chiba and S. Kakimoto, *J. Fac. Sci. Hokkaido Univ. Ser. III Chem.*, **4**, 1 (1950).

2) R. Pappo, D. S. Allen, R. V. Lemieux and W. S. Johnson, *J. Org. Chem.*, **21**, 478 (1956).

3a) R. C. Cookson and N. S. Wariyar, *J. Chem. Soc.*, **1956**, 2302.

3b) K. Wiesner, Z. Valenta, J. F. King, R. K. Maudgal, L. G. Humber and S. Itô, *Chem. & Ind.*, **1957**, 173.

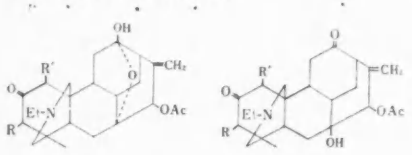
* In a previous paper[1], it has been reported that the hydrolysis of II gave miyaconine which was obtained also from I by the same hydrolysis. But the infrared spectrum of the former was different from that of the latter.

4) S. Kakimoto, This Bulletin, **32**, 349 (1959).

5) K. Wiesner, S. Itô and Z. Valenta, *Experientia*, **14**, 167 (1958).

closely related ring structures with these alkaloids.

Above all, it has been reported that selenium dehydrogenation of II gives phenanthrene and anthracene[6]. If anthracene ring occurred without rearrangement in the course of dehydrogenation, this fact, above consideration and the partial structures may lead possible structures for I and II as follows:



(I) R=O R'=H₂ (II)

As for the α-diketone system, R=O is more probable than R'=O**. The infrared absorption of I or II is similar*** to that of kobusine diacetate which has an allylic acetate function[7]. It is suggested that the acetyl group in I and II covers an allylic hydroxyl group which is observed generally in alkaloids of the atisine group. Some experimental studies in order to confirm the above considerations are in progress.

The authors wish to express their deep thanks to Professor Harusada Suginome, President of Hokkaido University, for his exceedingly kind direction throughout this work.

Department of Chemistry
Faculty of Science
Hokkaido University, Sapporo

6) H. Suginome and S. Kakimoto, This Bulletin, **32**, 352 (1959).

** In the molecular model of II, the active methylene group concerning the aldol condensation is more plausible R' than R.

*** In the comparison of infrared spectra of kobusine and kobusine diacetate, and II and III, similar shifts of the peaks were observed in the region of 870~930 cm^{-1}. These data will be reported in a later paper.

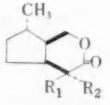
7) T. Okamoto, *Chem. Pharm. Bull. Japan*, **7**, 44 (1959).

The Structure of Matatabilactone

By Takeo Sakan, Akira Fujino, Fujio Murai, Akio Suzui and Yasuo Butsugan

(Received August 18, 1959)

In the preceding communication[1], the authors presented the structural formula of dihydronepetalactone for matatabilactone which was isolated as one of the physiologically active components for the Felidae animals from the leaves of *Actinidia polygama* Miq. (Matatabi). This estimation was principally based on the fact that two known epimeric nepetalinic acids were obtained by the oxidation of the corresponding hydroxy acid with potassium permanganate. It was pointed out that the alternative formula, i. e., that of isoiridomyrmecin(Ia)[2] or iridomyrmecin (Ib)[2] was unlikely to be the case because of the quite clear differences among the $\nu_{C=O}$ values in the infrared spectra of these substances. The examination thereafter has, however, led to some new informations in regard to the structural problem.



Ia $R_1=CH_3$, $R_2=H$

Ib $R_1=H$, $R_2=CH_3$

A hydroxy acid, $C_{10}H_{18}O_3$(II) of m. p. 109~110°C (*Anal.* Found: C, 63.86; H, 9.72. Calcd: C, 64.49; H, 9.74%) was isolated when I (*Anal.* Found: C, 71.54; H, 9.88. Calcd. for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59%) was, after alkali hydrolysis, treated carefully with acetic acid. By vacuum sublimation II was converted into a lactone, m. p. 60°C, $[\alpha]_D^{31}$ −67.6° (c 0.10, carbon tetrachloride)(III), from which the hydrazide(IV) of II, m. p. 119~120°C (*Anal.* Found: N, 14.11. Calcd. for $C_{10}H_{20}O_2N_2$: N, 13.99%) was derived. The physical properties of II—IV are respectively very similar to those of the compounds of Ia series. The mixed fusion tests and the

1) T. Sakan, A. Fujino, F. Murai, Y. Butsugan and A. Suzui., This Bulletin, **32**, 315 (1959).

2) G. W. K. Cavill and H. D. Locksley, *Australian J. Chem.*, **10**, 352 (1957).

comparisons of the infrared spectra of the samples of III and IV proved their identities with those that have been found by the Australian chemists. The authors are deeply indebted to Dr. G. W. K. Cavill for his kind offers.

It was difficult to seperate II completely from I, and accordingly, the residual part is as yet non-crystalline. Although attempts to obtain the other component in a pure state have been up to now without success, it is likely that matatabilactone is a mixture of Ia and Ib.

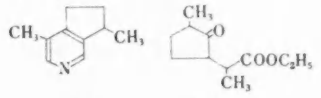
Institute of Polytechnics
Osaka City University
Kita-ku, Osaka

The Synthesis of Actinidine

By Takeo SAKAN, Akira FUJINO, Fujio MURAI, Akio SUZUI and Yasuo BUTSUGAN

(Received August 18, 1959)

Actinidine(I)[1], a basic effective component for the Felidae animals in *Actinidia polygama* Miq. (Matatabi), was synthesized from ethyl α-(3-methyl-2-oxo-cyclopentyl)-propionate(II)[2] as follows.



(I) (II)

The cyanohydrin of II was dehydrated to a cyanoester(III), b. p. 106~120°C/2 mmHg by the action of thionyl chloride in the presence of pyridine. The position of the double bond in III is not conclusive, and both possible isomers seem to have been actually produced. Attempts to separate them with alkali or ethoxide solution resulted in failure. On acid or alkali hydrolysis of III, the dihydroxy-pyridine derivative(IV), m. p. 167~168°C (*Anal.* Found: C, 66.71; H, 7.32; N, 7.77. Calcd. for $C_{10}H_{13}O_2N$: C, 67.02; H, 7.31; N, 7.82%) was obtained. Chlorination of IV with phosphorus oxychloride and successive catalytic hydrogenation of the dechloro-compound (oil) afforded DL-actinidine(V), b.p. 100~103°C/12 mmHg (picrate: m. p. 142~143°C). V was then resolved into an optically active form through the mono-salt of dibenzoyltartaric acid. The less soluble salt in absolute ethanol yielded, on regeneration of the base, a laevorotatory oil(VI), $[\alpha]_D^{31}$ −8.01° (c 2.17, chloroform), the infrared spectrum of which was in all respects identical with that of natural actinidine. Identity between the picrates of VI, m.p. 146~147°C, and of I, was also established through the mixed melting point determination and the comparison of the infrared spectra.

Institute of Polytechnics
Osaka City University
Kita-ku, Osaka

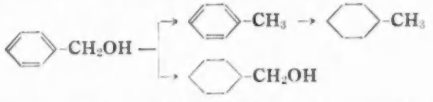
1) T. Sakan, A. Fujino, F. Murai, Y. Butsugan and A. Suzui, This Bulletin, **32**, 315 (1959).
2) R. L. Jones and R. P. Linstead, *J. Chem. Soc.*, **1936**, 616.

Hydrogenation and Hydrogenolysis. II[1]. *Selective Hydrogenation of Benzyl Alcohol, Methylphenylcarbinol and Benzohydrol to the Corresponding Saturated Carbinols*

By Shigeo NISHIMURA

(Received August 28, 1959)

Benzyl alcohol may be catalytically reduced either to methylcyclohexane through toluene, absorbing 4 mol. of hydrogen, or to cyclohexylcarbinol, absorbing 3 mol. of hydrogen:



Under mild conditions the two reactions compete, the former usually predominating.

The palladium catalyst in the presence of a trace of a mineral acid is preferred

1) Part I of this series: S. Nishimura and K. Mori, This Bulletin, **32**, 103 (1959).

TABLE I. MOLES OF HYDROGEN ABSORBED BY BENZYL ALCOHOL IN THE PRESENCE OF PLATINUM OXIDE-PLATINUM BLACK

Solvent	Catalyst g.	Compound, g. Benzyl alcohol (0.541)	Methylphenyl carbinol (0.611)	Benzohydrol (0.533)
EtOH, 30 cc. + HCl, 2 drops	0.2	3.96	3.98	7.04
AcOH 30 cc.	〃	3.95	3.87	6.73
EtOH, 30 cc. + AcOH, 0.2 cc.	〃	3.47		
〃 + AcOH, 0.1 cc.	〃	3.29		
〃 + AcOH, 0.03 cc.	0.1	3.16		
〃 + AcOH, 0.02 cc.	0.2	3.10	3.08	6.10

TABLE II. HYDROGENATION OF PHENYLCARBINOLS TO CYCLOHEXYLCARBINOLS IN THE PRESENCE OF PLATINUM OXIDE-PLATINUM BLACK

Compound	Amount g.	Solvent	Catalyst g.	Time hr.	Moles of H_2 absorbed mol./mol.	Product
Benzyl alcohol	3.24	EtOH, 30 cc. + AcOH, 0.05 cc.	1.0	7	3.06	Cyclohexylcarbinol (88%), (106~107°C/ 52 mm.), n_D^{25} 1.4622
Methylphenyl-carbinol	3.66	〃	〃	6	3.07	Cyclohexylmethyl-carbinol (86%), (91~ 92°C/21 mm.), n_D^{20} 1.4656
Benzohydrol	3.68	〃	〃	9	6.10	Dicyclohexylcarbinol (89%), (160~161°C/ 22 mm.), (62~63°C)

for the selective reduction of benzyl alcohol to toluene because of its high activity for the hydrogenolysis and of its low activity for the hydrogenation of the benzene nucleus. Adkins et al. carried out this hydrogenation, using various preparations of nickel-on-kieselguhr catalysts, but the highest yield of cyclohexylcarbinol was only 34%[2]. With Raney nickel toluene is obtained as the main product along with less than 20% of cyclohexylcarbinol[3-6].

With the platinum oxide catalyst, methylcyclohexane was the main product in the presence of a trace of hydrochloric acid or in acetic acid as indicated by the moles of hydrogen absorbed (Table I).

From the results reported previously[1], it was expected that benzyl alcohol could be quantitatively hydrogenated with platinum oxide to cyclohexylcarbinol best in neutral ethanolic solution, but under this condition benzyl alcohol absorbed practically no hydrogen. However, it was found that addition of acetic acid causes the absorption of hydrogen, and that the hydrogen absorption decreases with the decrease of the added acetic acid with no great depression of the rate of hydrogenation, until 3 mol. is absorbed in the presence of the trace of acetic acid, the results being summarized in Table I with those obtained with methylphenylcarbinol and benzohydrol. Thus, in the presence of a very small amount of acetic acid, the phenylcarbinols can be hydrogenated without difficulty to give nearly quantitative yields of the corresponding saturated carbinols[7] (Table II). Triphenylcarbinol was reduced only very slowly and the hydrogenation could not be completed.

With platinized Raney nickel, which is an excellent catalyst for the selective hydrogenation of furfuryl alcohol to tetrahydrofurfuryl alcohol and of cinnamyl alcohol to 3-phenyl-1-propanol[1], benzyl alcohol gave only a 20% yield of cyclohexylcarbinol.

All the hydrogenations, except those with platinized Raney nickel (100°C, 70 atm.), were carried out at the ordinary temperature and pressure. The substance to be hydrogenated was added after

2) H. Adkins and L. W. Covert, *J. Phys. Chem.*, **35**, 1684 (1931).
3) Hilly, *Bull. soc. chim.*, [5], **7**, 371 (1940).
4) L. Palfray, ibid., [5], **7**, 407 (1940).
5) B. Gauthier, *Ann. chim.*, [11], **20**, 647 (1945).
6) N. S. Tikhomirova-Sidrova, *Zhur. Obshchei Khim.*, **25**, 1504 (1955); *Chem. Abstr.*, **50**, 4825*h* (1956).

7) Under similar conditions cholest-4-en-3-ols can be hydrogenated to cholestan-3-ols almost quantitatively: C. W. Shoppee et al., *J. Chem. Soc.*, **1957**, 3107.

platinum oxide had been shaken with hydrogen for about thirty minutes[8].

The author wishes to express his hearty thanks to Professor Y. Urushibara for his kind advice.

Department of Chemistry
Faculty of Science
The University of Tokyo
Hongo, Tokyo

8) Freshly reduced platinum oxide-platinum black often catalyzes the hydrogenolysis even in neutral solution, but loses completely such activity after being shaken with hydrogen for about thirty minutes. The activity is recovered by the addition of a trace of hydrochloric acid. This is probably caused by platinum nitrate or basic nitrates remaining in traces in platinum oxide, which may liberate nitric acid when reduced with hydrogen, but, when the resulting material is shaken with hydrogen once again, the nitric acid is reduced to ammonia and the catalyst loses the activity for the hydrogenolysis.

Dialkylthioboronates

By Nobuyuki Ashikari

(Received September 7, 1959)

Many organo boron compounds are known to be effective catalysts for vinyl-polymerization[1-3]. Accordingly, several dialkylthioboronates have been prepared for testing the catalytic activity. It was found that though the activites of the compounds as polymerization catalysts were low, they reacted in a characteristic manner with ammonia. These compounds are new substances, and the synthetic method and some properties of them are described in this paper.

The only known dialkylthioboronate is dimethylthioboronate[4], $(CH_3)_2BSCH_3$, which was prepared by the interaction of methylmercaptan and tetramethyl diborane.

$$2CH_3SH + B_2H_2(CH_3)_4 = 2(CH_3)_2BSCH_3 + 2H_2$$

In the present studies, the dialkylthioboronates have been prepared by reaction between dialkylboron chloride and the sodium salt of mercaptan. While alcohols react readily with dialkylboron chloride to produce dialkylboronous esters[2], mercaptans do not react at least at room temperature. Dialkylthioboronate reacts readily with ammonia to produce a white solid at about $-60°C$, which appears to be an unstable 1 : 1 addition product. This product easily decomposes to dialkylamino borine, R_2BNH_2, on distillation. The reaction is considered to be as follows:

$$R_2BSR' \xrightarrow{\text{liq. } NH_3} R_2BSR' : NH_3$$
$$\xrightarrow{\text{distill.}} R_2BNH_2 + R'SH$$

The details of this aspect will be reported in the near future.

Experimental and Results. — In a 300 cc. three necked round-bottomed flask, fitted with a mechanical stirrer with a mercury seal, a reflux condenser, and a dropping funnel, were placed about 100 cc. of anhydrous ether and the various amonts of sodium shown in Table I. To the mixture,

Table I. Yields of R_2BSR'

R in R_2BCl	Wt., g.	R in $R'SH$[a]	Na, g.	Product, g.	Yield, %[b]
iso-C_3H_7	33	C_2H_5	10	18	30.0
n-C_4H_9	45	C_2H_5	10	30	40.0
n-C_4H_9	30	*iso*-C_3H	7	16	36.6
n-C_4H_9	31	*n*-C_4H_9	6	34	38.0

a) The amount of R'SH is 25 g. in each experiment.
b) The yield was calculated from R'SH employed.

25 g. of mercaptan was dropped slowly, with stirring. After completion of addition, the system was heated for about three hours, and the mixture was cooled to room temerature. The unchanged sodium was removed, and about 100 cc. of ethereal solution containing a certain amount of dialkylboron chloride (shown in Table I) was added slowly from the dropping funnel. The reaction proceeds as follows:

$$R_2BCl + R'SNa = R_2BSR' + NaCl$$

After the dropping had been completed, the mixture was heated for about four hours. The solvent was distilled off, and further distillation was carried out under reduced pressure. The products were redistilled for measurements of physical constants. The results are shown in Table II.

1) G. S. Kolesnikov and L. S. Fedorova, *Izv. AN. USSR*, No. 2, 236 (1957).
2) J. Furukawa et al., *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **61**, 728 (1958).
3) N. Ashikari, *J. Polymer Sci.*, **28**, 641 (1958).
4) A. B. Burg and R. I. Wagner, *J. Am. Chem. Soc.*, **76**, 3307 (1954).

TABLE II. PHYSICAL CONSTANTS OF R_2BSR'

R_2BSR'	b.p., °C	d_4^{20}	Calcd. B%	Found B%[c]
$(iso\text{-}C_3H_7)_2BSC_2H_5$	80/20 mm.	0.8490	6.96	7.04
$(n\text{-}C_4H_9)_2BSC_2H_5$	142/60 mm.	0.8400	5.91	6.11
$(n\text{-}C_4H_9)_2BS(iso\text{-}C_3H_7)$	74/4 mm.	0.8525	5.50	5.58
$(n\text{-}C_4H_9)_2BS(n\text{-}C_4H_9)$	78/3 mm.	0.8318	5.14	5.42

c) Quantitative analysis of boron was carried out by Synder's method[5].

Dialkylthioboronate is a colorless liquid having an unpleasant odor and is oxidized slowly in air. It seems, however, to be stable in cold water.

The Electrical Communication Laboratory
Nippon Telegraph and Telephone
Public Corporation
Musashino-shi, Tokyo

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Calculated Thermodynamic Properties of Trimethylchlorosilane

By Kazuhiro SHIMIZU and Hiromu MURATA

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The vibrational assignment of trimethylchlorosilane has been revised, based on a normal coordinate treatment as a fourteen body problem[1]. The probable values of the wave numbers of the normal vibrations were used to calculate the values of the heat content, free energy, entropy and heat capacity for the ideal gaseous state at 1 atmospheric pressure (rigid rotator, harmonic oscillator approximation). The bond distances and the interbond angles in the previous Table I[1] and the Hirschfelder formula[2] were used to calculate the product of the principal moments of inertia, $I_aI_bI_b = 3.85961\ 10^{-113}$ g^3 cm^6. The molecular weight used was 108.652 and the symmetry number was 3. The three torsional vibrational frequencies of the methyl groups belong to the species a_2 and e. No information about their frequencies has been given. Therefore, the total contributions of the translational, rotational and vibrational frequencies are listed in Table I, except those of the three unknown methyl torsional modes. When the contributions of the three ones are evaluated, they have to be added.

TABLE I. HEAT CAPACITY, FREE ENERGY AND HEAT CONTENT OF TRIMETHYLCHLOROSILANE FOR THE IDEAL CASEOUS STATE AT 1 ATMOSPHERIC PRESSURE (cal. deg^{-1} mol^{-1}), EXCEPT THE CONTRIBUTIONS OF THE THREE METHYL TORSIONAL FREQUENCIES

T°K	$(H^0-E_0^0)/T$	$-(F^0-E_0^0)/T$	S^0	C_p^0
100	9.39	49.03	58.43	12.67
200	12.59	56.54	69.13	18.79
273.15	14.87	60.72	75.59	23.47
300	15.72	62.24	77.96	25.23
400	18.89	67.19	86.08	31.43
500	21.95	71.74	93.69	36.75
600	24.80	75.99	100.79	41.20
700	27.41	80.02	107.43	44.96
800	29.82	83.76	113.57	48.21
900	32.02	87.47	119.50	51.04
1000	34.05	91.01	125.05	53.51

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Osaka Municipal Technical Research Institute
Kita-ku, Osaka

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2) J. O. Hirschfelder, *J. Chem. Phys.*, **8**, 431 (1940).